

Supporting Information

Selective CO₂ Electrochemical Reduction Enabled by a Tricomponent Copolymer Modifier on a Copper Surface

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1. Materials

The second-generation ruthenium metathesis catalyst $[(H_2IMes)(PCy_3)(Cl)_2Ru=CHPh]$ was generously provided by Umicore, and the third-generation ruthenium metathesis catalyst was prepared according to the reported procedure.¹ For polymerization, tetrahydrofuran was dried by passing through an activated alumina column and then distilled over sodium under an argon atmosphere. The solvent was further bubbled with N_2 to remove any remaining oxygen and stored over activated molecular sieves in a glovebox.

Deuterated solvents were purchased from Cambridge Isotopes Laboratories, Inc. and used as received.

Copper foil ($\geq 99.9999\%$, Puratronic®, thickness: 0.5 mm, AA42975-FI) was purchased from Alfa Aesar. Phosphoric acid (85%, 99.99% metals basis), potassium carbonate (99.995%) were purchased from Sigma-Aldrich. Water was purified by a Milli-Q Advantage A10 Water Purification System (Millipore) with specific resistance of $18.2\text{ M}\Omega\cdot\text{cm}$ at $25\text{ }^\circ\text{C}$.

Potassium bicarbonate electrolyte ($KHCO_3(aq)$, 0.1 M) was prepared by sparging an aqueous solution of potassium carbonate ($K_2CO_3(aq)$, 0.05 M) with CO_2 for at least 3 hours prior to electrolysis, which converts K_2CO_3 into $KHCO_3$ and saturates the electrolyte solution with CO_2 .

2. Instrument

Ambient temperature NMR spectra were recorded on a Varian 400 MHz or Bruker 400 MHz NMR spectrometer. Chemical shifts (δ) were given in ppm and referenced against residual solvent signals.

SEC data were collected using two Agilent PLgel MIXED-B 300×7.5 mm columns with 10 μ m beads, connected to an Agilent 1260 Series pump, a Wyatt 18-angle DAWN HELEOS light scattering detector, and Optilab rEX differential refractive index detector. Online determination of dn/dc assumed 100% mass elution under the peak of interest. The presence of charged groups in PILs results in unreliable MW characterization via SEC. To overcome such a problem, we used tetrahydrofuran with 10 mM LiNTf₂ as an additive as the mobile phase.²

X-ray photoelectron spectroscopy (XPS) data were collected using a Surface Science Instruments M-Probe ESCA controlled by Hawk Data Collection software (Service Physics, Bend OR; V7.04.04). The monochromatic x-ray source was the Al K α line at 1486.6 eV, directed at 35° to the sample surface (55° off normal). Emitted photoelectrons were collected at an angle of 90° with respect to the sample surface (0° off normal) by a hemispherical analyzer. The angle between the electron collection lense and X-ray source is 35°. Low-resolution survey spectra were acquired between binding energies of 1-1100 eV. Higher-resolution detailed scans, with a resolution of ~ 0.8 eV, were collected on individual XPS lines of interest. The sample chamber was maintained at $< 2 \times 10^{-9}$ Torr. The XPS data were analyzed using the Hawk Data Analysis software (V7.04.04). Copper foils were store in a nitrogen-filled glovebox before XPS measurements.

All SEM images were recorded on a ZEISS 1550VP FESEM instrument, equipped with in-lens SE, below-lens SE, variable pressure SE and Robinson-type BSE detectors. EDX measurements were done on an Oxford X-Max SDD X-ray Energy Dispersive Spectrometer (EDS) system.

All AFM images were recorded on a Bruker Dimension Icon using the ScanAsyst mode. A scanassyst-air cantilever was used with a spring constant of 0.4 N/m and a resonant frequency of 70 kHz. AFM images were acquired at a scan rate of 0.494 Hz, applying a peak force of 1.2 nN over 5 μ m with 1024 samples per line or 15 μ m with 2048 samples per line.

High-resolution mass spectra were obtained with a JEOL JMS-600H High Resolution Mass Spectrometer. Matrix-assisted laser desorption ionization (MALDI) mass spectra were obtained with an Autoflex MALDI TOF/TOF instrument (Bruker). Trace elemental analysis was conducted using an

Agilent 8800 ICP-MS.

3. Electrochemical measurement

Chronoamperometry measurements were carried out in a custom-made PEEK flow cell setup similar to the one reported³ using a copper foil as the working electrode and a platinum foil as the counter electrode. The cathode compartment was separated from the anode compartment by a Selemion AMV anion-exchange membrane (AGC Engineering Co.). All potentials were measured versus a leakless Ag/AgCl reference electrode (Innovative Instruments) with an outer diameter of 5 mm that was inserted into the cathode compartment. The reference electrode was calibrated against ferrocenecarboxylic acid in a 0.2 M phosphate buffer solution at pH 7.0 (+0.239 V vs. Ag/AgCl).

All electrochemical measurements were carried out using a BioLogic VSP-300 potentiostat. Prior to electrolysis experiments, linear scan voltammetry was conducted from the open-circuit potential to -1.05 V vs RHE at a scan rate of 20 mV/s in order to reduce any oxidized copper. Potentiostatic electrochemical impedance spectroscopy (PEIS) measurements were then carried out to determine the Ohmic resistance of the flow cell. The impedance measurements were carried out at frequencies ranging from 1 Hz to 1 MHz to measure the solution resistance.⁴ A Nyquist plot was plotted and in the high-frequency part a linear fit was performed, and the axis intersection was calculated. The value of this intersection represents the Ohmic resistance of the cell. Typically, resistances ranging from 55 to 65 Ω were measured.

All chronoamperometric experiments were performed for 64 min at 25 °C using CO₂-saturated 0.1 M KHCO₃ as electrolyte. The potentiostat was set to compensate for 85 % of the Ohmic drop, with the remaining 15 % being compensated for after the measurements. The effluent gas stream coming from the flow cell (5 sccm) was flowed into the sample loops of a gas chromatograph (GC-FID/TCD, SRI 8610C, in Multi Gas 5 configuration) equipped with HayeSep D and Molsieve 5A columns. Methane, ethylene, ethane and carbon monoxide were detected by a methanizer-flame ionization detector (FID) and the hydrogen was detected by a thermal conductivity detector (TCD). Every 4.2 minutes, 2 mL of gas was sampled to determine the concentration of gaseous products. The peak areas of standard mixed gases of hydrogen, methane, carbon monoxide, and ethylene were used to make the standard curves.

After electrolysis, the liquid products in both catholytes and anolytes were quantified by ¹H NMR. For ¹H NMR, solutions containing 90% electrolyte and 10% D₂O (v/v) with internal standard (phenol

and dimethylsulfoxide) were prepared and measured using a water suppression technique on a Bruker 400 MHz NMR spectrometer. To avoid problems arising from the analyte and internal standard having different T1s, we used the same spectral acquisition parameters for all quantification spectra. (NS=32, P1=6.0 μ s, D1=8.0 μ s) Peak areas of products were compared to internal standards to make standard curves.⁴

Faradaic efficiencies (FE) were calculated from the following equation:

$$FE = \frac{(nF \times z)}{Q} \times 100\%$$

Here, n is the amount of a specific product, z is the number of electrons to reduce one molecule of a specific product, F is Faradaic constant, and Q is the total amount of charge passed.

All potentials were converted from the Ag/AgCl scale to the reversible hydrogen electrode (RHE) scale by using $E_{RHE} = E_{(Ag/AgCl)} - 0.197 - 0.059 \times pH$, where E_{RHE} , $E_{(Ag/AgCl)}$ measured and pH are potential vs RHE, measured potential vs Ag/AgCl reference electrode and pH of the electrolyte (6.8).

4. Data for electrochemical CO₂ reduction

Table S1. Faradaic efficiencies and current densities toward different products produced during CO₂ reduction on copolymer modified polycrystalline copper electrodes*

Polymer	j(mA/cm ²)	Faradaic efficiency (%)						
		CO	CH ₄	C ₂ H ₄	H ₂	EtOH	HCO ₂ H	PrOH
Cu	5.22 ± 0.58	0.5 ± 0.1	25.6 ± 2.9	22.3 ± 2.3	39.7 ± 4.6	5.9 ± 1.3	1.8 ± 0.8	1.4 ± 0.4
1	12.2 ± 3.1	0.0	1.5 ± 1.5	0.0	94.6 ± 1.7	0.0	0.7 ± 0.4	0.0
2	3.90 ± 0.52	1.0 ± 0.2	14.1 ± 1.1	5.3 ± 0.3	69.3 ± 2.3	0.0	6.6 ± 0.1	0.0
3	2.75 ± 0.83	2.8 ± 2.2	14.0 ± 2.7	21.5 ± 4.0	37.8 ± 6.4	3.4 ± 0.6	11.1 ± 3.9	2.6 ± 0.7
4	4.04 ± 0.77	0.4 ± 0.3	33.1 ± 5.0	19.0 ± 5.7	34.1 ± 4.2	3.9 ± 2.1	3.8 ± 1.5	1.8 ± 1.2
5	4.64 ± 0.61	0.5 ± 0.3	28.1 ± 6.0	25.5 ± 3.7	33.6 ± 6.5	6.0 ± 0.2	1.1 ± 0.7	1.1 ± 0.7
6	4.92 ± 0.79	1.1 ± 0.6	22.3 ± 8.6	30.4 ± 3.1	32.5 ± 3.1	9.3 ± 3.5	1.0 ± 0.4	1.0 ± 0.3
7	4.11 ± 0.28	1.2 ± 0.5	4.7 ± 0.9	49.5 ± 2.1	16.5 ± 4.5	16.0 ± 4.4	2.2 ± 0.8	3.2 ± 1.5
8	4.66 ± 0.90	0.7 ± 0.3	1.9 ± 1.9	55.6 ± 1.2	11.9 ± 1.2	17.4 ± 1.5	1.9 ± 1.0	4.3 ± 0.5
9	5.06 ± 0.46	0.4 ± 0.2	2.8 ± 1.2	53.8 ± 3.8	19.2 ± 2.3	15.5 ± 2.4	0.9 ± 0.4	2.1 ± 0.8
10	3.68 ± 0.03	1.0 ± 0.4	11.5 ± 3.7	36.8 ± 1.5	35.0 ± 1.2	9.5 ± 2.9	1.8 ± 0.6	1.3 ± 0.7
11	2.56 ± 0.60	2.3 ± 0.4	8.7 ± 3.0	31.7 ± 4.3	36.2 ± 6.8	4.3 ± 1.2	9.0 ± 1.9	2.2 ± 0.6
12	4.51 ± 0.44	0.5 ± 0.3	25.0 ± 4.9	20.4 ± 0.7	44.8 ± 1.5	5.2 ± 2.6	1.4 ± 0.3	1.0 ± 0.5
13	4.49 ± 0.21	0.6 ± 0.1	5.7 ± 0.6	59.8 ± 3.4	21.9 ± 0.4	11.8 ± 1.9	1.3 ± 0.6	1.2 ± 0.8
block-8	4.05 ± 0.22	0.6 ± 0.1	14.1 ± 2.0	34.5 ± 2.4	30.5 ± 3.2	11.0 ± 0.7	2.4 ± 0.5	3.0 ± 0.1

*Electroreduction conducted in CO₂ saturated 0.1 M KHCO₃ at an applied potential of −1.08 V_{RHE} for 64 min, unless otherwise noted. The experiment with polymer **1**-modified Cu was conducted at −1.04 V_{RHE}.

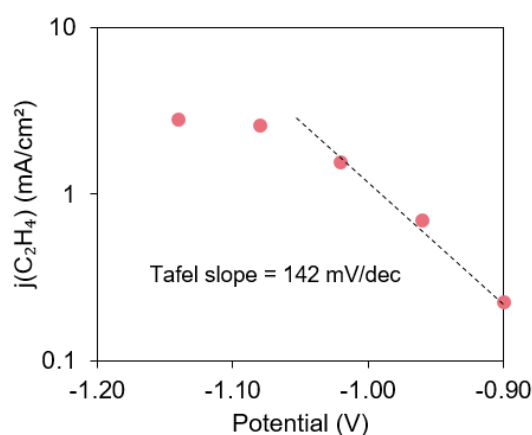


Figure S1. Partial ethylene current densities and its Tafel slope

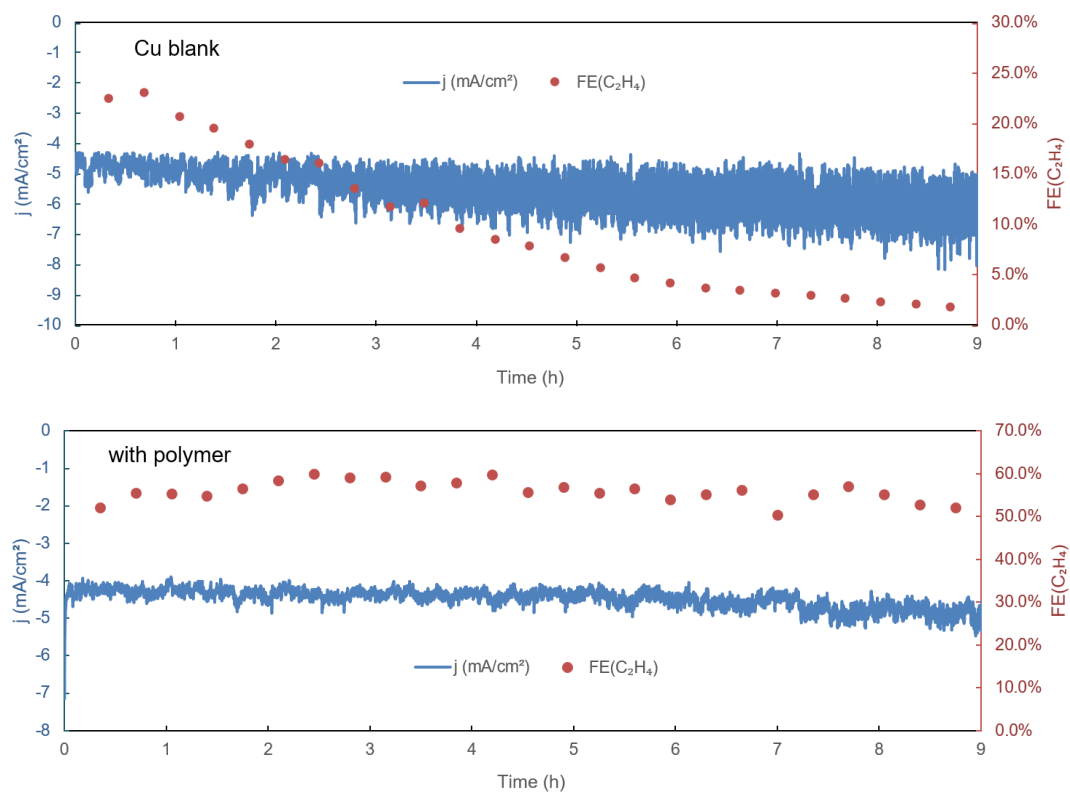


Figure S2. Stability in the FE of C₂H₄ and the current density for Cu blank (top) and Cu modified with polymer **13** (bottom) at $-1.08\text{ V}_{\text{RHE}}$ during a 9 h test.

6. AFM study of the film thickness

Preparation of vapor-deposited Cu electrode (Cu-PVD): 100 nm of Cu was deposited at 2 Å/s on Si(111) substrate in a three-source physical vapor deposition chamber, following a procedure described in the literature.⁵ The Cu thin film was then coated with polymer **8** by the general spin coating method mentioned above. After spin coating, a scratch was made by hand in the polymer film with a razor blade, which was confirmed not to damage the Cu underneath the polymer.

The surfaces mentioned above were studied by AFM. Cu-PVD has a smooth surface with a root-mean-square roughness $R_q = 1.0$ nm (Fig. S3a), and the polymer **8** coated surface has a rough surface with $R_q = 19.6$ nm (Fig. S3b). The surface inside the scratch showed $R_q = 2.2$ nm (Fig. S3c), which is similar to the Cu-PVD (a small amount of residual polymer is likely the cause of a slightly rougher surface). The AFM image on the edge of the scratch was further taken. The R_q calculated confirmed that one side is mainly the exposed copper while the other side is the polymer-coated surface.

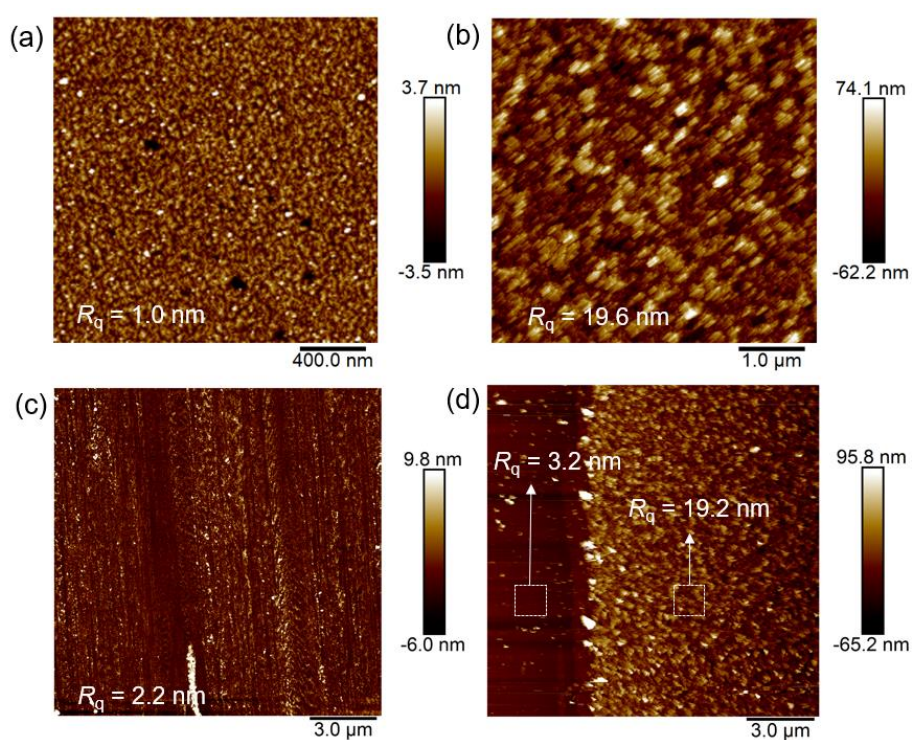


Figure S3. AFM images of (a) Cu-PVD; (b) Cu-PVD spin-coated with polymer **8**; (c, d) sample (b) scratched with a razor blade.

5. Characterization of the Cu surface underneath

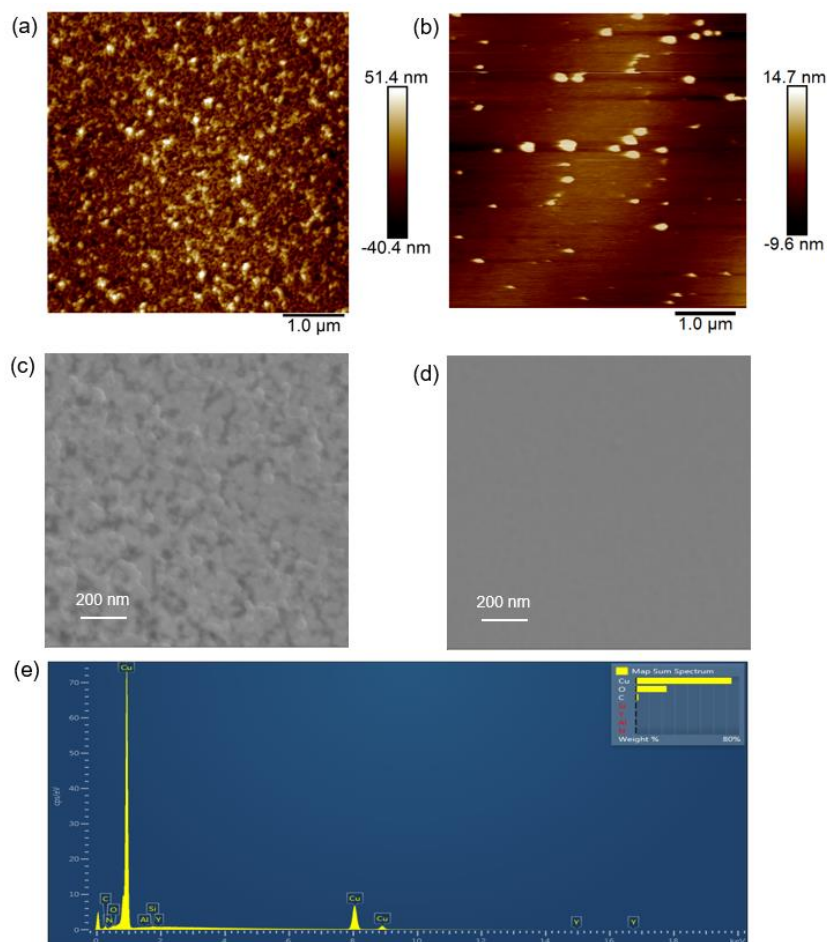


Figure S4. AFM images of the post-electrolysis Cu electrode coated with polymer **8**, (a) before solvent extraction; (b) after extraction of the polymer layer with organic solvents; SEM images of the post-electrolysis Cu electrode coated with polymer **8**, (c) before solvent extraction; (d) after extraction of the polymer layer with organic solvents; (e) EDX spectrum of the surface of (d).

6. XPS Study

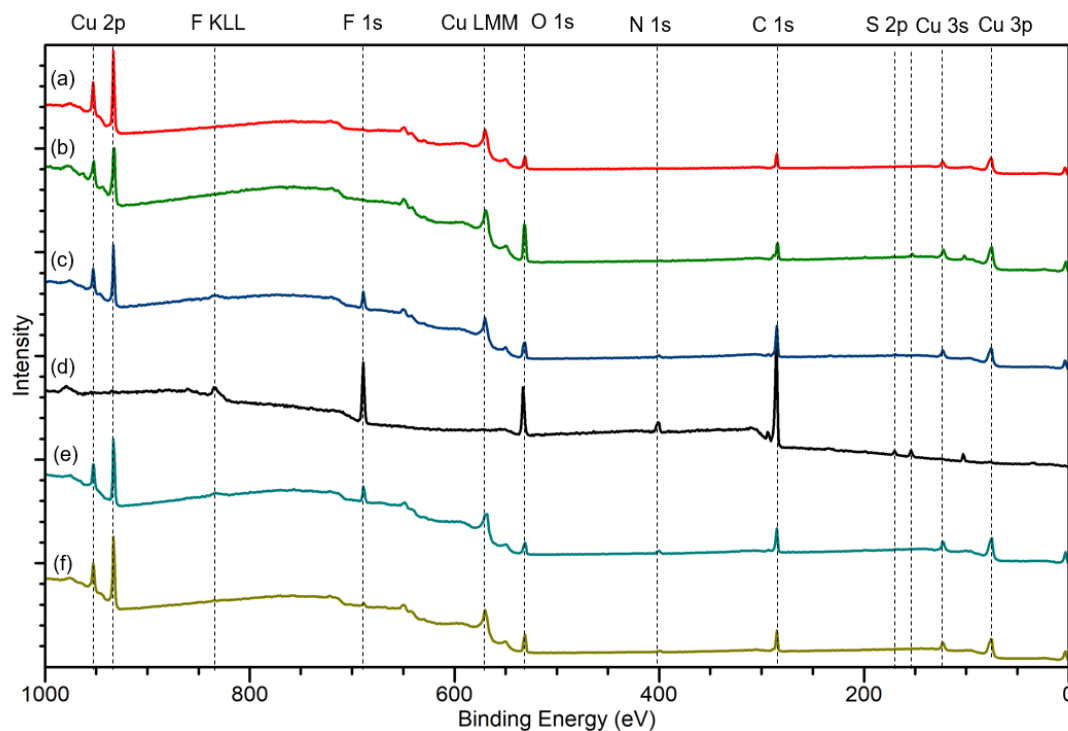


Figure S5. XPS spectra of (a) electropolished Cu before CO₂RR; (b) electropolished Cu after CO₂RR; (c) Cu electrode coated with diluted polymer **8** solution (0.5 mg/mL) before CO₂RR; (d) Cu electrode coated with polymer **8** solution (5 mg/mL) after CO₂RR; (e) Cu electrode coated with polymer **8** solution (5 mg/mL) after CO₂RR with the removal of polymer layer by dissolving the polymer with 30 mL of methanol; (f) Cu electrode coated with polymer **8** solution (5 mg/mL) before CO₂RR with the removal of polymer layer by dissolving the polymer with 30 mL of methanol.

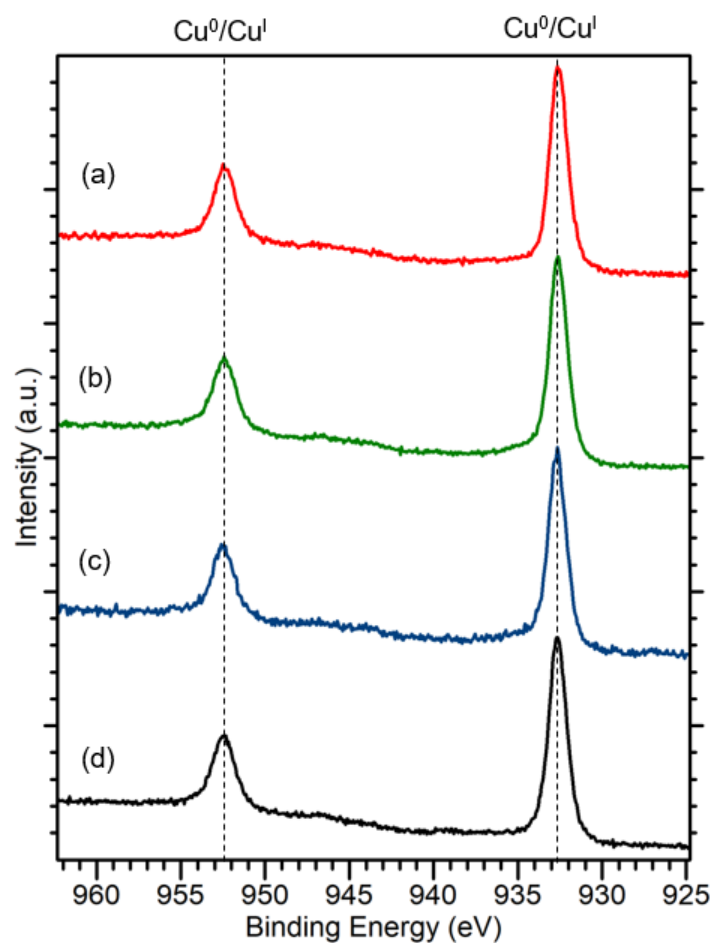


Figure S6. XPS spectra of Cu 2p electron taken for (a) electropolished Cu before CO_2RR ; (b) electropolished Cu after CO_2RR (c) Cu electrode coated with diluted polymer **8** solution (0.5 mg/mL) before CO_2RR ; (d) Cu electrode coated with polymer **8** solution (5 mg/mL) after CO_2RR with removal of polymer layer by dissolving the polymer with 30 mL of methanol

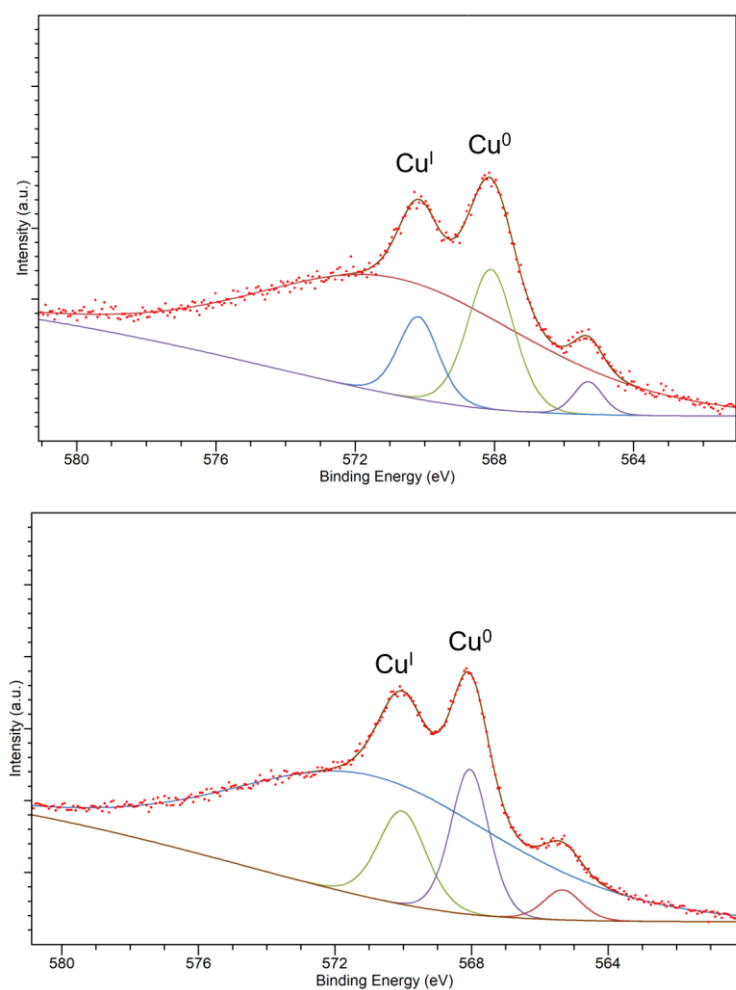


Figure S7. Cu LMM spectra of Cu electrode after CO₂RR (top), and the Cu electrode modified with polymer **8** after CO₂RR with the removal of polymer layer by methanol solvent (bottom).

7. Contact angle measurement

A ramé-hart contact angle goniometer was used for surface angle measurement. The images were analyzed with ImageJ with the help of the Drop Analysis' plugin developed at the École polytechnique fédérale de Lausanne (EPFL).

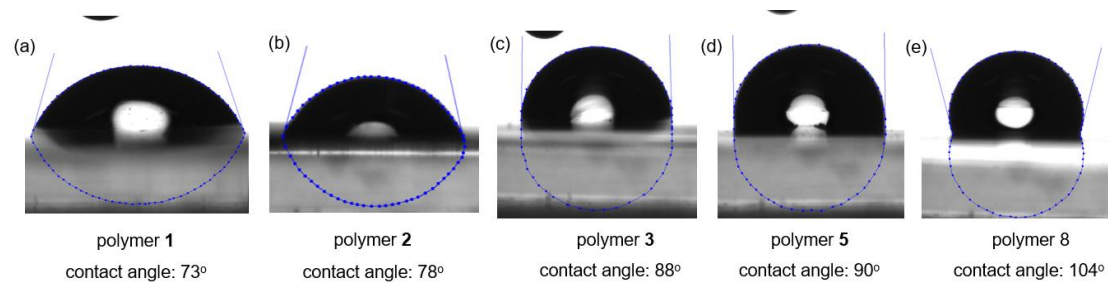


Figure S8. Contact angle measurement of water on polymer-coated copper surfaces

8. Additional SEM studies

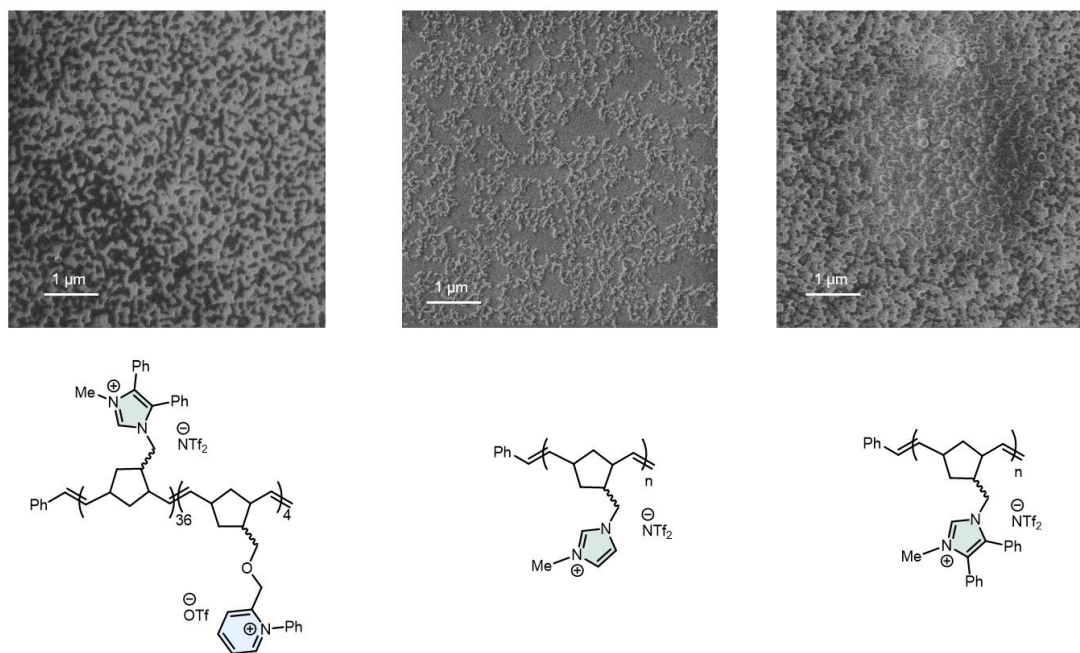


Figure S9. Ex-situ SEM image of the Cu foil electrode modified with different polymers before the electrocatalysis

9. Simulation models and simulation methods

9.1. Simulation models

The polymers were built strictly according to the experiments, as shown in Figure 2. The distribution of branches was random (according to the experiment) and propagated using probabilities. Torsion angles were generated randomly. The electrode surface consists of 6 layers of 14×12 Cu (111) surface with 1008 atoms. Anions (NTf_2^- and OTf^-) were added to balance the charge to neutral. 43 CO_2 molecules were added, corresponding to a mol fraction of 0.007.⁶ Finally, water molecules were inserted to fill up the space. A typical simulation snapshot of polymer + water / Cu is shown in Figure S10.

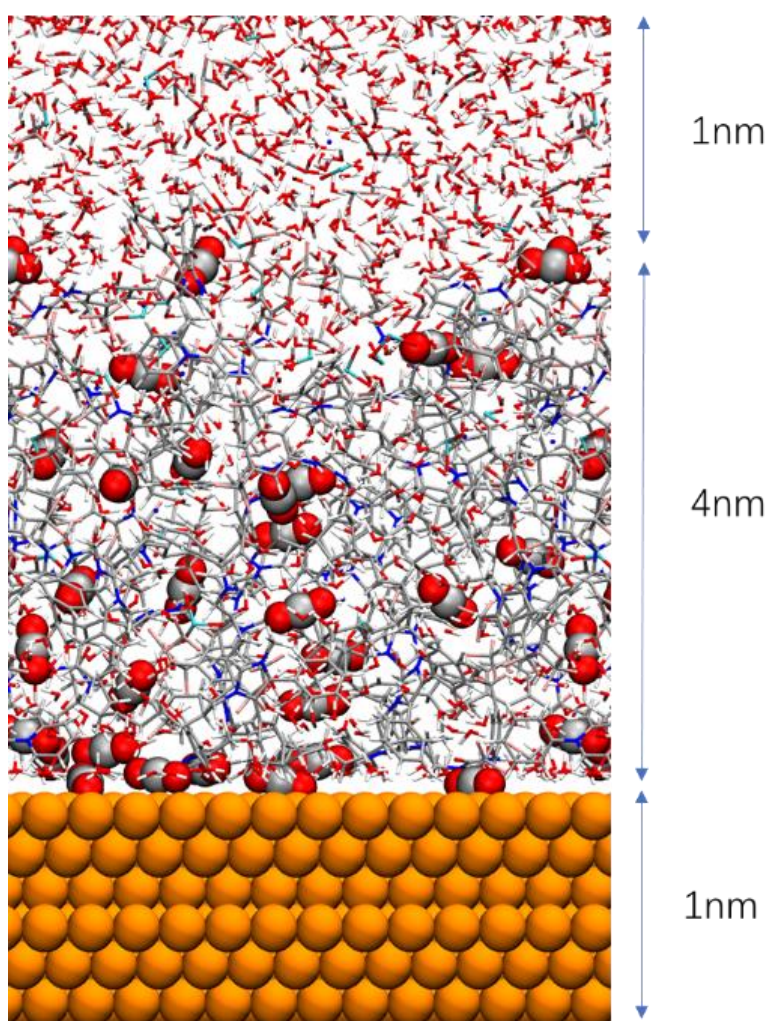


Figure S10. The interface structure after 12 ns molecular dynamics simulation of polymer 8 + water / Cu interface. The colors are: Cu in orange, C in gray, O in red, N in blue, F in pink, S in cyan, and H in white.

9.2. Density functional theory calculations

Electronic structure calculations were performed within the density functional theory (DFT) framework, as implemented in the Vienna ab initio simulation program (VASP 5.4.4), a plane-wave pseudopotential package, with the projector augmented wave (PAW) method to account for core-valence interactions. The exchange and correlation energies were calculated using the Perdew, Burke, and Ernzerhof (PBE) functional within the generalized gradient approximation (GGA). Spin polarization did not have an appreciable effect on the overall energies. The PBE-D3 method was employed to correct van der Waals interaction. We used plane-wave cutoff energy of 400 eV and the first order Methfessel-Paxton scheme with a smearing width of 0.2 eV. Dipole corrections were applied along the z-axis. The energy minimization criterion was that all forces on free atoms be < 0.02 eV/Å.

9.3. Molecular Mechanics Calculations

Molecular Mechanics calculations were performed by using Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) version 12Dec20. In MM simulation, the Universal Force Field (UFF) was used to describe the interatomic interaction with vdW parameters revised to reproduce the DFT calculations (as shown in Table S2 and the fragments in Figure S11). The time step of the molecular dynamics (MD) simulation is 1 fs. In water/Cu interface and polymer + water /Cu interface simulations, canonical ensemble (NVT) simulation was carried out with Nose Hoover thermostat at 300K with the damping factor of 100 fs. In polymer simulations, isothermal–isobaric ensemble (NPT) simulation was carried out with Nose Hoover thermostat at 300 K with a damping factor of 100 fs for temperature and a damping factor of 1000 fs for pressure.

9.4. Analysis of results

9.4.1 CO₂ in the inner Helmholtz plane

A CO₂ molecule is considered to be in the inner Helmholtz plane if its center of mass is within 5 Å from the Cu surface. The trajectory of 1 ns NVT MD simulation was used for analysis. The statistics were estimated from the standard deviation.

9.4.2 Charge on surface Cu

The charge of the outmost (first layer) Cu atoms were analyzed from QEq calculations. The trajectory of 1 ns NVT MD simulation was used for analysis. The statistics were estimated from the standard deviation.

9.4.3 Volume ratio

The volume of polymer (V_0) was calculated from NPT simulations of polymer only. The volume

polymer in the electrolyte (V) was calculated from NVT simulation of polymer + water/Cu interface by using solvent-accessible surfaces, in which the grid interval was set to 0.75 Å, vdW scaling factor to 1.0, and initial solvent radius to 1.4 Å (represent for water). The ratio (V/V_0) was employed to characterize the porosity in the manuscript.

9.4.4 Electric field

The electrostatic potential was computed along the z-direction. The potential is calculated by first summing the charges per slice and then integrating twice of this charge distribution. Periodic boundaries in z-direction are not considered. Reference of potential is taken to be the left side of the box. The electric field (E) was calculated from the potential divided by unit charge.

10. Simulation results

10.1. Simulation models

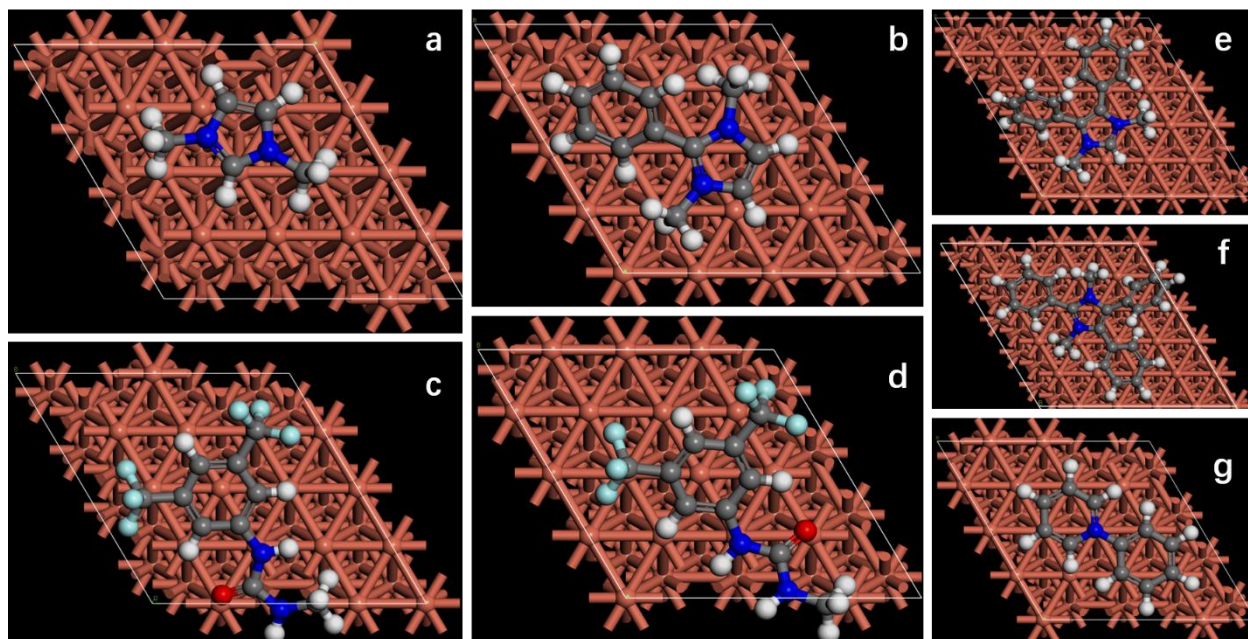


Figure S11. The fragments considered in DFT calculations

Table S2. Comparison of the binding energies (in eV) of fragments in Figure S1 between DFT and MM.

	a	b	c	d	e	f	g
DFT	-2.74	-2.75	-2.50	-3.46	-1.48	-1.35	-2.21
MM	-2.59	-2.61	-2.30	-3.33	-1.31	-1.23	-2.39

10.2. Convergence of potential energy

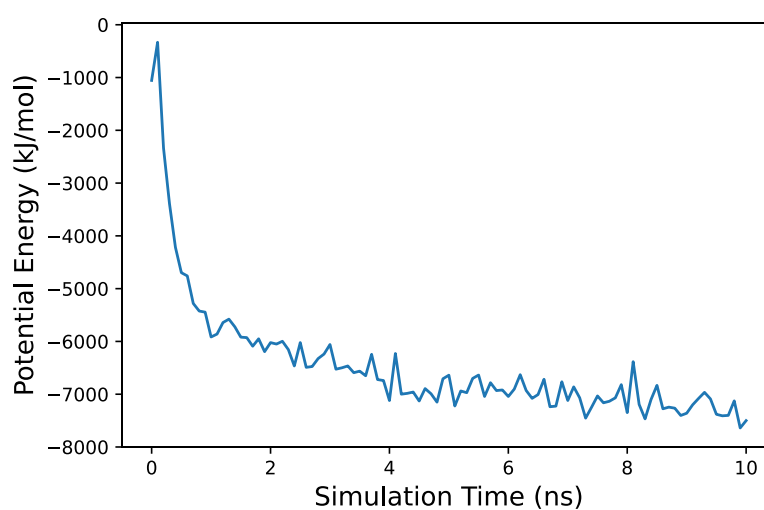


Figure S12. The potential energy of 10 ns simulation of polymer **8** + water / Cu at 300K.

10.3. Correlation of experimental FEs with calculated concentrations

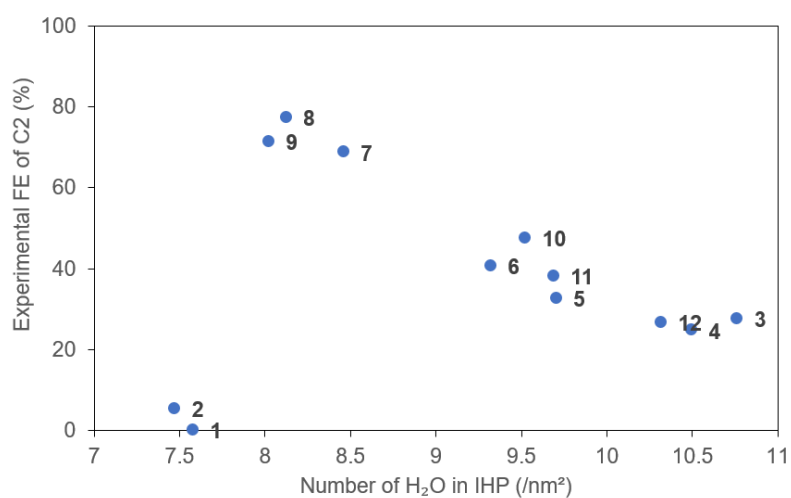


Figure S13. The relationship of the number of H₂O molecules (/nm²) from MD with the experimental Faradic efficiencies of C₂⁺ products.

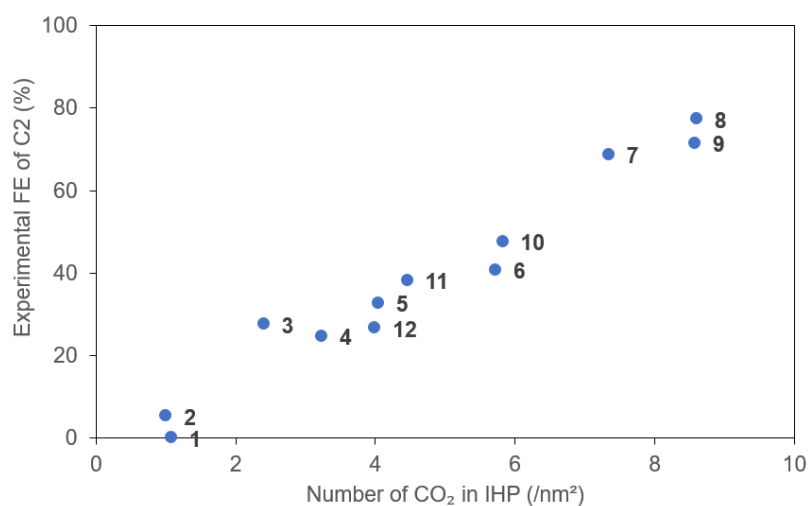


Figure S14. The relationship of the number of CO₂ molecules (/nm²) from MD with the experimental Faradic efficiencies of C₂⁺ products.

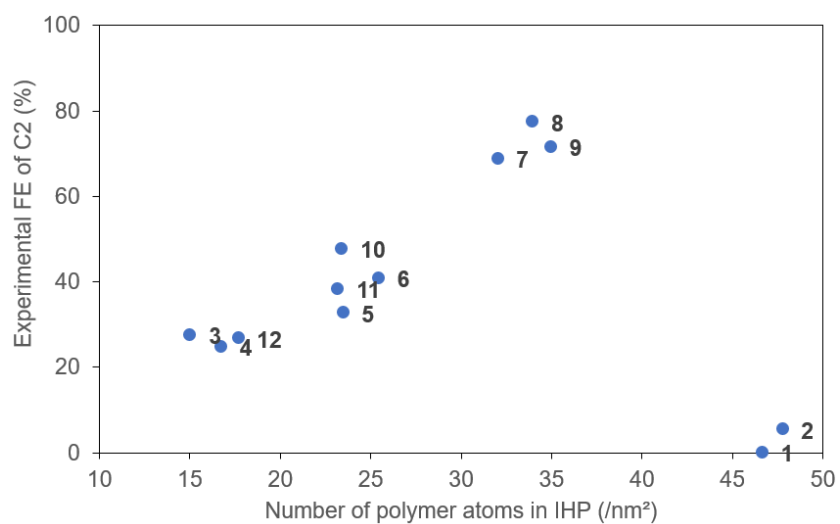
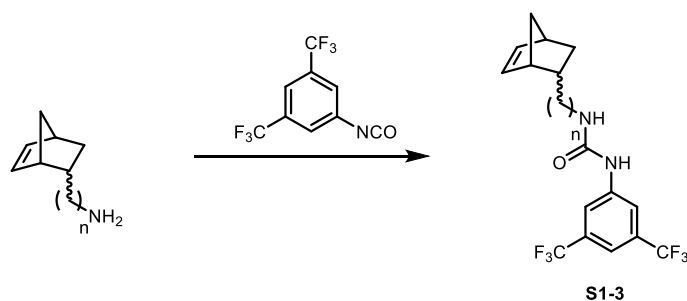


Figure S15. The relationship of the number of polymer atoms ($/\text{nm}^2$) from MD with the experimental Faradic efficiencies of C_2^+ products.

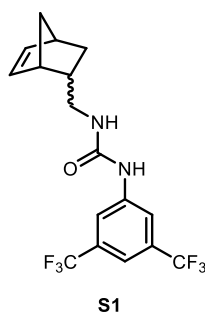
11. Synthesis and characterization data of monomers

General procedure A for synthesizing urea containing monomer

2-(bicyclo[2.2.1]hept-5-en-2-yl)ethan-1-amine⁷ (685 mg, 5.0 mmol) was added to 20 mL of anhydrous tetrahydrofuran in a 100 mL round-bottomed flask. This stirred solution was cooled to 0 °C using an ice water bath. 3,5-Bis(trifluoromethyl)phenyl isocyanate (1.23 g, 4.8 mmol) in 20 mL of tetrahydrofuran was added dropwise over a period of 15 minutes. The mixture was allowed to warm to room temperature and stirred at ambient temperatures for 12 hours. Upon completion of the reaction, the mixture was concentrated in vacuum. The residue was purified by flash column chromatography on silica gel to yield the desired product as a white solid (85% yield).



S1 was synthesized from 5-norbornene-2-methylamine via general procedure A.



endo:exo = 85 : 15

S1: White solid. R_f = 0.45 (hexane/ethyl acetate = 5:1).

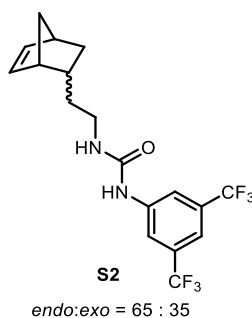
¹H NMR (400 MHz, Acetonitrile-*d*₃) δ 7.96 (s, 2H, aryl-*H*), 7.82 (d, J = 18.4 Hz, 1H, N-*H*), 7.48 (s, 1H, aryl-*H*), 6.14 (dd, J = 5.8, 3.0 Hz, 0.85H, *endo* vinyl-*H*), 6.08 – 6.02 (m, 0.30H, *exo* vinyl-*H*), 5.96 (dd, J = 5.8, 2.9 Hz, 0.85H, *endo* vinyl-*H*), 5.73 (t, J = 5.2 Hz, 0.15H, *exo* N-*H*), 5.62 (t, J = 5.7 Hz, 0.85H, *endo* N-*H*), 3.34 – 3.10 (m, 0.3H, *exo* CH₂NH), 2.98 (ddd, J = 12.9, 6.9, 5.8 Hz, 0.85H, *endo* aliphatic-*H*), 2.86 – 2.77 (m, 1.85H, aliphatic-*H*), 2.75 (td, J = 3.6, 1.7 Hz, 0.85H, *endo* aliphatic-*H*), 2.62 (s, 0.15H, *exo* bridgehead-*H*), 2.30 – 2.18 (m, 0.85H, *endo* aliphatic-*H*), 1.81 (ddd, J = 11.5, 9.1, 3.9 Hz, 0.85H, *endo* aliphatic-*H*), 1.54 (dt, J = 12.9, 6.4, 3.2 Hz, 0.15H, *exo* aliphatic-*H*), 1.37 (dq, J = 8.2, 2.1

Hz, 1H, aliphatic-*H*), 1.30 – 1.13 (m, 1.30H, aliphatic-*H*), 0.53 (ddd, $J = 11.5, 4.4, 2.6$ Hz, 0.85H, *endo* aliphatic-*H*).

^{13}C NMR (101 MHz, Acetonitrile- d_3) δ 155.52, 142.69, 137.89, 137.25, 136.87, 132.64, 131.93 (q, $J = 32.9$ Hz), 124.13 (q, $J = 271.9$ Hz), 118.42, 114.96 (q, $J = 4.0$ Hz), 49.66, 45.36, 45.18, 44.62, 44.27, 42.91, 42.21, 40.02, 39.63, 30.89, 30.19.

HRMS (ESI): Calcd for $\text{C}_{17}\text{H}_{17}\text{F}_6\text{N}_2\text{O}^+$ ($\text{M}+\text{H}^+$): 379.1240, found: 379.1257.

S2 was synthesized from 2-(bicyclo[2.2.1]hept-5-en-2-yl)ethan-1-amine⁷ via general procedure A.



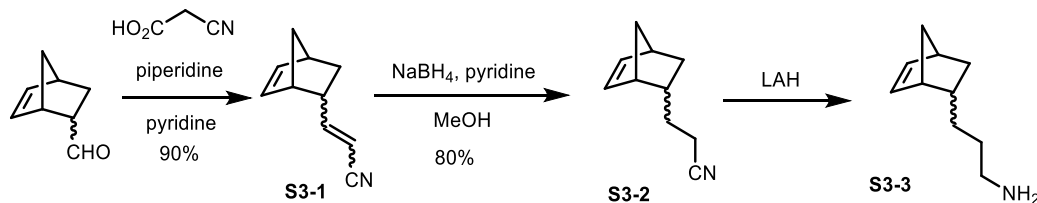
S2: White solid. $R_f = 0.45$ (hexane/ethyl acetate = 5:1).

^1H NMR (400 MHz, Acetonitrile- d_3) δ 7.98 (s, 2H, aryl-*H*), 7.48 (s, 1H, aryl-*H*), 6.10 (dd, $J = 5.8, 3.0$ Hz, 0.65H, *endo* vinyl-*H*), 6.06 (dd, $J = 5.7, 3.0$ Hz, 0.35H, *exo* vinyl-*H*), 6.00 (dd, $J = 5.7, 2.9$ Hz, 0.35H, *exo* vinyl-*H*), 5.92 (dd, $J = 5.8, 2.9$ Hz, 0.65H, *endo* vinyl-*H*), 5.78 – 5.63 (m, 1H, N-*H*), 3.22 (dd, $J = 7.1, 4.0$ Hz, 0.7H, *exo* CH_2NH), 3.15 (td, $J = 7.3, 5.5$ Hz, 1.3H, *endo* CH_2NH), 2.76 (s, 1H, bridgehead-*H*), 2.72 (s, 0.65H, *endo* bridgehead-*H*), 2.50 (s, 0.35H, *exo* bridgehead-*H*), 2.01 (dtt, $J = 15.2, 7.3, 3.7$ Hz, 0.65H, *endo* aliphatic-*H*), 1.84 (ddd, $J = 11.3, 9.0, 3.9$ Hz, 0.65H, *endo* aliphatic-*H*), 1.68 – 1.46 (m, 0.70H, *exo* $\text{CH}_2\text{CH}_2\text{NH}$), 1.38 – 1.07 (m, 4.35H, aliphatic-*H*), 0.49 (ddd, $J = 11.3, 4.4, 2.6$ Hz, 0.65H, *endo* aliphatic-*H*).

^{13}C NMR (101 MHz, Acetonitrile- d_3) δ 156.02, 143.27, 137.95, 137.62, 137.12, 133.15, 125.93, 132.31 (q, $J = 32.9$ Hz), 124.58 (q, $J = 271.8$ Hz), 118.72 (q, $J = 4.2$ Hz), 115.24 (p, $J = 3.9$ Hz), 50.18, 47.21, 46.25, 45.88, 43.38, 42.79, 39.96, 39.87, 37.45, 37.00, 36.96, 35.81, 33.49, 32.86.

HRMS (ESI): Calcd for $\text{C}_{18}\text{H}_{19}\text{F}_6\text{N}_2\text{O}^+$ ($\text{M}+\text{H}^+$): 393.1396, found: 393.1401.

A full assignment of ^1H NMR and ^{13}C NMR can be found in Figure S59 and Figure S60, based on its COSY, NOESY, and HSQC.

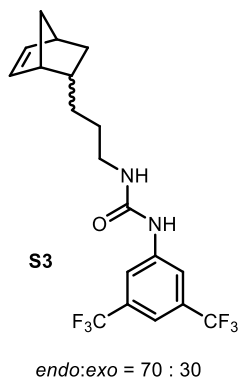


S3-1 A mixture of 5-norbornene-2-carboxaldehyde (6.1 g, 50 mmol) and 10 mL of piperidine was added to a solution of cyanoacetic acid (9.84 g, 116 mmol) in 20 mL of anhydrous pyridine. The reaction mixture was heated on a water bath until carbon dioxide evolution ceased, then cooled and poured into a mixture of ice and hydrochloric acid. The reaction product was extracted with diethyl ether (3×50 mL), washed with a 10% solution of Na_2CO_3 (3×50 mL) and water, and dried over MgSO_4 . Then the solvent was removed carefully to avoid loss of volatile product. The residue was purified by flash column chromatography (pentane/diethyl ether = 10:1) on a very short silica gel to yield the desired product as a yellowish liquid (90% yield).

S3-2 An E/Z mixture of **S3-1** (5.3 g, 37 mmol) was dissolved in 48 mL of anhydrous MeOH and pyridine (1: 3 v/v). Then, NaBH_4 (2.08 g, 55 mmol) was added by portions with stirring. After refluxing for 2 h, the mixture turned colorless and was allowed to cool to room temperature and then poured into 100 mL of 10% aqueous HCl. The reaction product was extracted with diethyl ether (3×50 mL), washed with a 10% solution of Na_2CO_3 (3×50 mL) and water, and dried over MgSO_4 . Then the solvent was removed carefully to avoid loss of volatile product. The residue was purified by flash column chromatography (pentane/diethyl ether = 10:1) on a very short silica gel to yield the desired product as a yellowish liquid (80% yield).

S3-3 A stirred solution containing LiAlH_4 (2.5 g, 66 mmol) in 30 mL of dry THF was cooled in an ice bath. To this solution, a solution containing **S3-2** (2.2 g, 15 mmol) in 10 mL of dry THF was added dropwise over a period of 15 min. The stirring was continued at reflux for 2 h, then at room temperature for 20 h. After quenching excess LiAlH_4 by sequential addition of H_2O (2.5 mL), 15% NaOH solution (2.5 mL), and H_2O (7.5 mL), the mixture was stirred for 15 min. Anhydrous MgSO_4 was added and further stirred for 45 min. The mixture was filtered, and the residue was washed with diethyl ether. The filtrate was evaporated to give a crude product of **S3-3**, which was used in the next step without further purification.

S3 was synthesized from **S3-3** via general procedure A.



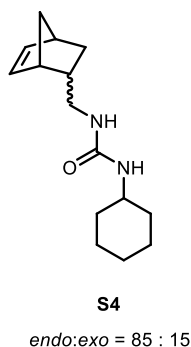
S3: White solid. R_f = 0.45 (hexane/ethyl acetate = 5:1).

^1H NMR (400 MHz, Methanol- d_4) δ 7.89 (s, 2H, aryl-*H*), 7.35 (s, 1H, aryl-*H*), 6.00 (dd, J = 5.7, 3.1 Hz, 0.7H, *endo* vinyl-*H*), 5.97 (dd, J = 5.8, 3.1 Hz, 0.3H, *exo* vinyl-*H*), 5.90 (dd, J = 5.7, 2.9 Hz, 0.3H, *exo* vinyl-*H*), 5.82 (dd, J = 5.8, 2.9 Hz, 0.7H, *endo* vinyl-*H*), 3.09 (dt, J = 16.4, 7.0 Hz, 1.7H, aliphatic-*H*), 2.66 (s, 1H, bridgehead-*H*), 2.62 (s, 0.7H, *endo* bridgehead-*H*), 2.40 (s, 0.3H, *exo* bridgehead-*H*), 1.97 – 1.84 (m, 0.7H, *endo* aliphatic-*H*), 1.76 (ddd, J = 11.3, 9.0, 3.9 Hz, 0.7H *endo* aliphatic-*H*), 1.55 – 0.96 (m, 7.2H, aliphatic-*H*), 0.41 (ddd, J = 11.2, 4.3, 2.6 Hz, 0.7H *endo* aliphatic-*H*).

^{13}C NMR (101 MHz, Methanol- d_4) δ 156.01, 142.06, 136.64, 136.40, 135.81, 131.77, 131.72 (q, J = 33.0 Hz), 123.43 (q, J = 271.8 Hz), 113.96, 49.10, 46.17, 45.18, 44.63, 42.35, 41.66, 39.70, 38.42, 38.34, 33.45, 32.65, 31.98, 31.69, 28.95, 28.71.

HRMS (ESI): Calcd for $\text{C}_{19}\text{H}_{21}\text{F}_6\text{N}_2\text{O}^+$ ($\text{M}+\text{H}^+$): 407.1553, found: 407.1557.

S4 was synthesized from 5-norbornene-2-methylamine (CAS: 95-10-3) and cyclohexyl isocyanate via general procedure A.

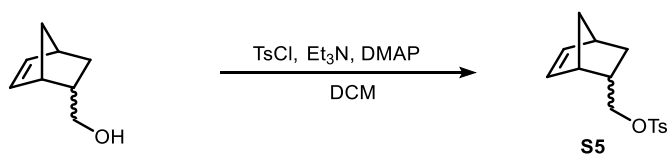


^1H NMR (400 MHz, Chloroform- d) δ 6.13 (dd, J = 5.8, 3.0 Hz, 0.85H, *endo* vinyl-*H*), 6.05 (td, J = 2.9, 0.8 Hz, 0.3H, *exo* vinyl-*H*), 5.95 (dd, J = 5.7, 2.9 Hz, 0.85H, *endo* vinyl-*H*), 5.51 (t, J = 5.6 Hz, 0.15H, *exo* N-*H*), 5.32 (t, J = 5.4 Hz, 0.85H, *endo* N-*H*), 5.27 (d, J = 8.2 Hz, 0.15H, *exo* N-*H*), 5.17 (d, J = 8.2

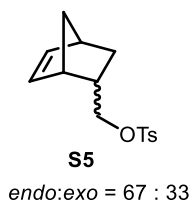
Hz, 0.85H, *endo* N-H), 3.62 – 3.45 (m, 1H, aliphatic-H), 3.25 (ddd, $J = 12.8, 6.9, 5.7$ Hz, 0.15H, *exo* aliphatic-H), 3.10 (ddd, $J = 13.0, 8.6, 5.6$ Hz, 0.15H, *exo* aliphatic-H), 2.95 (ddd, $J = 12.6, 6.8, 5.7$ Hz, 0.85H, *endo* aliphatic-H), 2.84 (dp, $J = 3.4, 1.6$ Hz, 0.85H, *endo* aliphatic-H), 2.77 (ddd, $J = 12.8, 9.0, 5.4$ Hz, 1.85H, aliphatic-H), 2.65 – 2.61 (m, 0.15H, *exo* aliphatic-H), 2.28 – 2.16 (m, 0.85H, *endo* aliphatic-H), 1.91 (dt, $J = 12.5, 3.7$ Hz, 2H, aliphatic-H), 1.82 (ddd, $J = 11.5, 9.1, 3.9$ Hz, 0.85H, *endo* aliphatic-H), 1.69 (dp, $J = 11.4, 3.8$ Hz, 2H, aliphatic-H), 1.59 (dt, $J = 13.1, 4.0$ Hz, 1H, aliphatic-H), 1.55 – 1.47 (m, 0.15H, *exo* aliphatic-H), 1.42 (dq, $J = 8.2, 2.1$ Hz, 0.85H, *endo* aliphatic-H), 1.39 – 1.26 (m, 2.3H, aliphatic-H), 1.26 – 1.20 (m, 1H, aliphatic-H), 1.12 (dtd, $J = 14.9, 11.8, 6.3$ Hz, 3.15H, aliphatic-H), 0.54 (ddd, $J = 11.5, 4.4, 2.5$ Hz, 0.85H, *endo* aliphatic-H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.33, 137.43, 136.43, 132.20, 49.48, 48.74, 45.53, 45.04, 44.39, 44.25, 44.17, 42.38, 39.81, 39.45, 34.02, 30.89, 30.15, 25.69, 25.03.

HRMS (ESI): Calcd for $\text{C}_{15}\text{H}_{25}\text{N}_2\text{O}^+$ ($\text{M}+\text{H}^+$): 249.1961, found: 249.1940.



At 0 °C, 5-norbornene-2-methanol (mixture of *endo* and *exo*, 4.96 g, 40.0 mmol), triethylamine (8.3 mL, 60.0 mmol), and 4-(dimethylamino)pyridine (0.98 g, 8.0 mmol) were dissolved in dichloromethane (120 mL). 4-Toluenesulfonyl chloride (9.88 g, 52.0 mmol) was added to the reaction mixture in portions. The reaction mixture was further stirred for 16 hours at room temperature. Upon completion of the reaction, it was quenched by aqueous NH_4Cl solution and extracted by dichloromethane. The organic layer was washed with water and brine, dried over MgSO_4 , and purified on silica gel chromatography (hexane/ethyl acetate = 20:1 to 10:1) to afford the product as a colorless liquid (83% yield). Note: *endo/exo* ratio might vary between different batches of commercial 5-norbornene-2-methanol.



S5: Colorless liquid. $R_f = 0.45$ (hexane/ethyl acetate = 10:1).

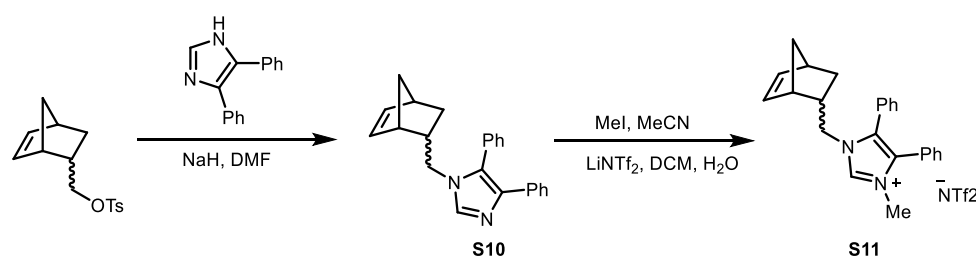
^1H NMR (400 MHz, Chloroform-*d*) δ 7.87 – 7.68 (m, 2H, aryl-H), 7.35 (ddt, $J = 7.8, 1.5, 0.7$ Hz, 2H,

aryl-*H*), 6.09 (dd, $J = 5.8, 3.1$ Hz, 0.67H, *endo* vinyl-*H*), 6.07 – 6.01 (m, 0.66H, *exo* vinyl-*H*), 5.68 (dd, $J = 5.8, 2.9$ Hz, 0.67H, *endo* vinyl-*H*), 4.08 (dd, $J = 9.6, 6.4$ Hz, 0.33H, *exo* CH₂OTs), 3.91 (t, $J = 9.4$ Hz, 0.33H, *exo* CH₂OTs), 3.80 (dd, $J = 9.4, 6.3$ Hz, 0.67H, *endo* CH₂OTs), 3.56 (t, $J = 9.6$ Hz, 0.67H, *endo* CH₂OTs), 2.88 (s, 0.67H, *endo* bridgehead-*H*), 2.78 (s, 1H, bridgehead-*H*), 2.69 (s, 0.33H, *exo* bridgehead-*H*), 2.45 (s, 3H, CH₃), 2.43 – 2.34 (m, 0.67H, *endo* aliphatic-*H*), 1.79 (ddd, $J = 11.8, 9.3, 3.7$ Hz, 0.67H, *endo* aliphatic-*H*), 1.76 – 1.68 (m, 0.33H, *exo* aliphatic-*H*), 1.42 (dq, $J = 8.4, 2.1$ Hz, 0.67H, *endo* aliphatic-*H*), 1.30 (ddd, $J = 8.8, 2.6, 1.5$ Hz, 0.33H, *exo* aliphatic-*H*), 1.27 – 1.19 (m, 1H, aliphatic-*H*), 1.15 (dt, $J = 8.8, 1.6$ Hz, 0.33H, *exo* aliphatic-*H*), 1.07 (ddd, $J = 11.9, 4.5, 3.5$ Hz, 0.33H, *exo* aliphatic-*H*), 0.43 (ddd, $J = 11.8, 4.5, 2.6$ Hz, 0.67H, *endo* aliphatic-*H*).

¹³C NMR (101 MHz, Chloroform-*d*) δ 144.63, 137.96, 137.06, 135.95, 133.19, 131.74, 129.84, 129.80, 127.86, 74.39, 73.77, 49.27, 44.79, 43.61, 43.33, 42.15, 41.54, 38.17, 37.99, 29.31, 28.62, 21.64.

HRMS (ESI): Calcd for C₁₅H₁₉O₃S⁺ (M+H⁺): 279.1049, found: 279.1037.

General procedure B for synthesizing imidazolium containing monomer

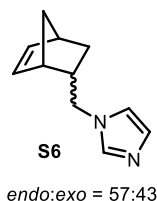


Under a nitrogen atmosphere, sodium hydride (520 mg, 60%, 13 mmol) was dispersed in anhydrous DMF (40 mL). Under stirring, 4,5-diphenyl-1*H*-imidazole (220 mg, 12 mmol) was added in several portions. The reaction mixture was further stirred at room temperature for 2 hours. A DMF solution of (bicyclo[2.2.1]hept-5-en-2-yl)methyl 4-methylbenzenesulfonate (3.06 g, 11 mmol) was added dropwise to the reaction mixture. The mixture was further stirred at 80 °C for 16 hours. After cooling to room temperature, it was quenched and diluted by water. Then it was extracted by ethyl acetate, washed with water and brine, dried over MgSO₄, and purified on silica gel chromatography (dichloromethane/ethyl acetate = 5:1) to afford the product **S10** as a white solid (75% yield).

Under a nitrogen atmosphere, 1-((bicyclo[2.2.1]hept-5-en-2-yl)methyl)-4,5-diphenyl-1*H*-imidazole (856 mg, 2.1 mmol) and methyl iodide (596 mg, 2.1 mmol) was dissolved in acetonitrile (10 mL) and heated to 70 °C for 12 hours. After evaporation of the solvent, the residue along with

bis(trifluoromethane)sulfonimide lithium salt (1.44 g, 5.0 mmol) were stirred in dichloromethane (10 mL) for 12 hours. Then it was concentrated and purified on silica gel chromatography (dichloromethane/acetone = 3:1) to afford the product **S11** as a white solid (75% yield).

S6 and **S7** were synthesized from imidazole via general procedure B.



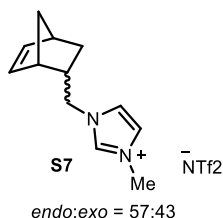
S6: Colorless liquid. R_f = 0.20 (hexane/ethyl acetate = 1:1).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.48 (s, 0.4H, *exo* aryl-*H*), 7.43 (s, 0.6H, *endo* aryl-*H*), 7.06 (s, 1H, aryl-*H*), 6.93 (s, 0.4H, *exo* aryl-*H*), 6.91 (s, 0.6H, *endo* aryl-*H*), 6.27 (dd, J = 5.8, 3.1 Hz, 0.6H, *endo* vinyl-*H*), 6.09 (dd, J = 5.7, 2.9 Hz, 0.4H, *exo* vinyl-*H*), 6.03 (ddd, J = 8.5, 5.7, 3.0 Hz, 1H, vinyl-*H*), 4.05 – 3.82 (m, 0.8H, *exo* CH_2N), 3.73 – 3.54 (m, 1.2H, *endo* CH_2N), 2.88 (s, 0.4H, *exo* bridgehead-*H*), 2.85 (s, 0.6H, *endo* bridgehead-*H*), 2.69 (s, 0.6H, *endo* bridgehead-*H*), 2.57 – 2.52 (s, 0.4H, *exo* bridgehead-*H*), 2.50 (dt, J = 10.2, 3.4 Hz, 0.6H, *endo* aliphatic-*H*), 1.87 (tdd, J = 15.3, 8.8, 4.2 Hz, 1H, aliphatic-*H*), 1.52 – 1.39 (m, 1H, aliphatic-*H*), 1.38 – 1.24 (m, 1.6H, aliphatic-*H*), 1.24 – 1.17 (m, 0.4H, *exo* aliphatic-*H*), 0.63 (ddd, J = 11.8, 4.5, 2.7 Hz, 0.6H, *endo* aliphatic-*H*).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.55, 137.20, 137.10, 137.00, 136.02, 131.59, 129.33, 129.23, 119.02, 118.86, 52.27, 50.96, 49.58, 44.84, 44.17, 44.09, 42.48, 41.86, 40.67, 40.49, 31.00, 30.10.

HRMS (ESI): Calcd for $\text{C}_{11}\text{H}_{15}\text{N}_2^+$ ($\text{M}+\text{H}^+$): 175.1230, found: 175.1244.

A full assignment of ^1H NMR and ^{13}C NMR could be found in Figure S46 and Figure S47, based on its COSY, NOESY, and HSQC.



S7: Colorless liquid. R_f = 0.50 (dichloromethane/acetone = 5:1).

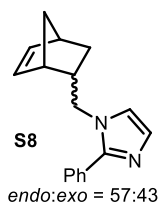
^1H NMR (400 MHz, Chloroform-*d*) δ 8.78 (t, J = 1.7 Hz, 0.43H, *exo* aryl-*H*), 8.70 (t, J = 1.7 Hz, 0.57H, *endo* aryl-*H*), 7.37 – 7.31 (m, 1.43H, aryl-*H*), 7.29 (t, J = 1.8 Hz, 0.57H, *endo* aryl-*H*), 6.30 (dd, J = 5.8,

3.1 Hz, 0.57H, *endo* vinyl-*H*), 6.12 (dd, $J = 5.7, 3.0$ Hz, 0.43H, *exo* vinyl-*H*), 6.06 (dd, $J = 5.7, 3.1$ Hz, 0.43H, *exo* vinyl-*H*), 6.01 (dd, $J = 5.8, 2.8$ Hz, 0.57H, *endo* vinyl-*H*), 4.26 – 4.11 (m, 0.86H, *exo* CH₂N), 3.94 (dd, $J = 1.7, 0.5$ Hz, 3H, CH₃), 3.87 (d, $J = 8.1$ Hz, 1.14H, *endo* CH₂N), 2.95 – 2.85 (m, 1H, bridgehead-*H*), 2.74 (s, 0.57H, *endo* bridgehead-*H*), 2.66 – 2.50 (m, 1H, aliphatic-*H*), 2.00 – 1.83 (m, 1H, aliphatic-*H*), 1.51 (dq, $J = 8.5, 2.1$ Hz, 0.57H, *endo* aliphatic-*H*), 1.49 – 1.28 (m, 2H, aliphatic-*H*), 1.28 – 1.20 (m, 0.57H, *endo* aliphatic-*H*), 0.65 (ddd, $J = 11.8, 4.4, 2.6$ Hz, 0.57H, *endo* aliphatic-*H*).

¹³C NMR (101 MHz, Chloroform-*d*) δ 139.38, 137.58, 136.08, 135.91, 135.59, 130.90, 123.82, 123.74, 122.37, 122.33, 121.40, 118.21, 55.02, 54.10, 49.58, 44.89, 44.09, 42.46, 41.96, 39.79, 39.77, 36.36, 30.73, 29.88.

HRMS (ESI): Calcd for C₁₂H₁₇N₂⁺ (M⁺): 189.1386, found: 189.1392.

S8 and **S9** were synthesized from imidazole via general procedure B.

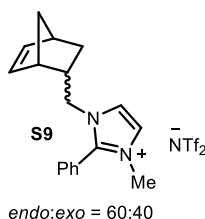


S8: Colorless liquid. $R_f = 0.25$ (hexane/ethyl acetate = 1:1).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.56 (ddt, $J = 6.9, 2.3, 1.0$ Hz, 2H, aryl-*H*), 7.49 – 7.34 (m, 3H, aryl-*H*), 7.18 – 6.98 (m, 1H, aryl-*H*), 6.10 (dd, $J = 5.8, 3.1$ Hz, 0.57H, *endo* vinyl-*H*), 6.04 (dd, $J = 5.7, 2.9$ Hz, 0.43H, *exo* vinyl-*H*), 5.98 (dd, $J = 5.7, 3.1$ Hz, 0.43H, *exo* vinyl-*H*), 5.53 (dd, $J = 5.8, 2.9$ Hz, 0.57H, *endo* vinyl-*H*), 4.09 (dd, $J = 13.9, 6.8$ Hz, 0.43H, *exo* CH₂N), 3.95 (dd, $J = 13.9, 9.3$ Hz, 0.43H, *exo* CH₂N), 3.81 (dd, $J = 13.9, 6.2$ Hz, 0.57H, *endo* CH₂N), 3.66 (dd, $J = 13.9, 9.4$ Hz, 0.57H, *endo* CH₂N), 2.83 – 2.72 (m, 1H, bridgehead-*H*), 2.60 (s, 0.57H, *endo* bridgehead-*H*), 2.47 – 2.34 (m, 1H, aliphatic-*H*), 1.88 – 1.75 (m, 1H, aliphatic-*H*), 1.39 (dq, $J = 8.3, 2.1$ Hz, 0.57H, *endo* aliphatic-*H*), 1.32 – 1.21 (m, 1H, aliphatic-*H*), 1.21 – 1.15 (m, 0.57H, *endo* aliphatic-*H*), 1.12 – 1.03 (m, 0.86H, *exo* aliphatic-*H*), 0.52 (ddd, $J = 11.7, 4.6, 2.6$ Hz, 0.57H, *endo* aliphatic-*H*).

¹³C NMR (101 MHz, Chloroform-*d*) δ 138.31, 137.17, 135.93, 131.60, 129.03, 128.93, 128.66, 128.62, 128.54, 128.52, 128.44, 128.38, 120.57, 120.42, 51.76, 50.67, 49.46, 44.73, 44.07, 43.82, 42.31, 41.72, 40.65, 40.33, 30.82, 30.10.

HRMS (ESI): Calcd for C₁₇H₁₉N₂⁺ (M+H⁺): 251.1543, found: 251.1570.



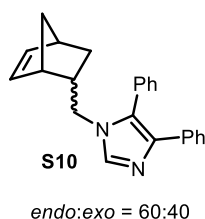
S9: White solid. R_f = 0.55 (dichloromethane/acetone = 5:1).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.78 – 7.63 (m, 3H, aryl-*H*), 7.60 – 7.52 (m, 2H, aryl-*H*), 7.50 (dd, J = 3.6, 2.2 Hz, 1H, aryl-*H*), 7.46 (dd, J = 4.9, 2.1 Hz, 1H, aryl-*H*), 6.10 (dd, J = 5.8, 3.1 Hz, 0.6H, *endo* vinyl-*H*), 6.06 (dd, J = 5.7, 2.9 Hz, 0.4H, *exo* vinyl-*H*), 6.00 (dd, J = 5.7, 3.1 Hz, 0.4H, *exo* vinyl-*H*), 5.41 (dd, J = 5.8, 2.9 Hz, 0.6H, *endo* vinyl-*H*), 4.09 (dd, J = 14.0, 7.0 Hz, 0.4H, *exo* CH_2N), 3.93 (dd, J = 14.0, 9.4 Hz, 0.4H, *exo* CH_2N), 3.83 – 3.60 (m, 4.2H, aliphatic-*H*), 2.79 (s, 1H, bridgehead-*H*), 2.66 (s, 0.6H, *endo* bridgehead-*H*), 2.48 – 2.36 (m, 1H, aliphatic-*H*), 1.93 – 1.71 (m, 1.8H, aliphatic-*H*), 1.42 (dt, J = 8.5, 2.2 Hz, 0.6H, *endo* aliphatic-*H*), 1.04 (dt, J = 12.0, 3.9 Hz, 0.4H, *exo* aliphatic-*H*), 0.97 – 0.90 (m, 0.4H, *exo* aliphatic-*H*), 0.47 (ddd, J = 11.9, 4.5, 2.6 Hz, 0.6H, *endo* aliphatic-*H*).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.30, 137.48, 135.49, 132.99, 130.78, 130.26, 130.13, 123.75, 121.75, 121.69, 53.79, 52.85, 49.54, 44.54, 43.88, 43.69, 42.28, 41.75, 39.60, 39.30, 35.99, 30.66, 29.99.

HRMS (ESI): Calcd for $\text{C}_{18}\text{H}_{21}\text{N}_2^+$ (M^+): 265.1699, found: 265.1715.

S10 and **S11** were synthesized from imidazole via general procedure B.



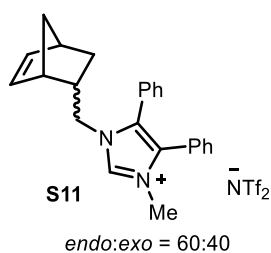
S10: White solid. R_f = 0.50 (dichloromethane/ethyl acetate = 1:1).

^1H NMR (500 MHz, Chloroform-*d*) δ 7.67 (s, 0.4H, *exo* aryl-*H*), 7.63 (s, 0.6H, *endo* aryl-*H*), 7.55 – 7.44 (m, 5H, aryl-*H*), 7.39 – 7.32 (m, 2H, aryl-*H*), 7.23 (dd, J = 8.4, 6.7 Hz, 2H, aryl-*H*), 7.19 – 7.13 (m, 1H, aryl-*H*), 6.17 (dd, J = 5.8, 3.1 Hz, 0.6H, *endo* vinyl-*H*), 6.06 (dd, J = 5.7, 2.9 Hz, 0.4H, *exo* vinyl-*H*), 6.00 (dd, J = 5.7, 3.1 Hz, 0.4H, *exo* vinyl-*H*), 5.67 (dd, J = 5.8, 2.9 Hz, 0.6H, *endo* vinyl-*H*), 3.93 (dd, J = 14.0, 6.7 Hz, 0.4H, *exo* CH_2N), 3.73 (dd, J = 14.0, 9.5 Hz, 0.4H, *exo* CH_2N), 3.62 (dd, J = 14.0, 6.4 Hz, 0.6H, *endo* CH_2N), 3.51 (dd, J = 14.0, 9.3 Hz, 0.6H, *endo* CH_2N), 2.80 (s, 1H, bridgehead-*H*), 2.66 (s, 0.6H, *endo* bridgehead-*H*), 2.49 (s, 0.4H, *exo* bridgehead-*H*), 2.33 – 2.21 (m, 0.6H, *endo* aliphatic-*H*),

1.80 (ddd, $J = 11.7, 9.2, 3.9$ Hz, 0.6H, *endo* aliphatic- H), 1.76 – 1.64 (m, 0.4H, *exo* aliphatic- H), 1.43 (dq, $J = 8.4, 2.2$ Hz, 0.6H, *endo* aliphatic- H), 1.31 (dt, $J = 8.9, 2.0$ Hz, 0.4H, *exo* aliphatic- H), 1.28 – 1.16 (m, 1H, aliphatic- H), 1.09 (dt, $J = 11.9, 3.5$ Hz, 0.8H, *exo* aliphatic- H), 0.53 (ddd, $J = 11.7, 4.5, 2.6$ Hz, 0.6H, *endo* aliphatic- H).

^{13}C NMR (126 MHz, Chloroform- d) δ 138.40, 137.21, 136.76, 136.62, 135.95, 131.55, 130.99, 130.86, 129.07, 129.05, 128.66, 128.60, 128.10, 128.09, 126.56, 126.48, 126.21, 126.18, 50.07, 49.55, 49.09, 44.62, 44.06, 43.79, 42.40, 41.69, 40.17, 39.88, 30.93, 30.28.

HRMS (ESI): Calcd for $\text{C}_{23}\text{H}_{23}\text{N}_2^+$ ($\text{M}+\text{H}^+$): 327.1856, found: 327.1884.



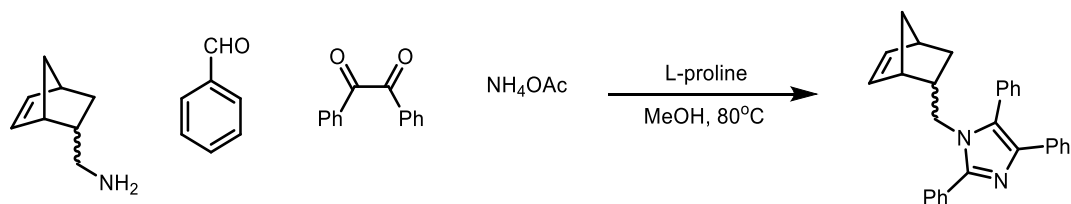
S11: White solid. $R_f = 0.80$ (dichloromethane/acetone = 2:1).

^1H NMR (400 MHz, Chloroform- d) δ 8.90 (s, 0.4H, *exo* aryl- H), 8.86 (s, 0.6H, *endo* aryl- H), 7.50 – 7.37 (m, 6H, aryl- H), 7.31 – 7.24 (m, 4H, aryl- H), 6.11 (dd, $J = 5.8, 3.1$ Hz, 0.6H, *endo* vinyl- H), 6.04 (dd, $J = 5.7, 2.9$ Hz, 0.4H, *exo* aryl- H), 6.00 (dd, $J = 5.7, 3.1$ Hz, 0.4H, *exo* aryl- H), 5.44 (dd, $J = 5.8, 2.9$ Hz, 0.6H, *endo* aryl- H), 4.25 – 4.04 (m, 0.8H, *exo* CH_2N), 3.90 – 3.77 (m, 4.2H, aliphatic- H), 2.81 (s, 0.4H, *exo* bridgehead- H), 2.78 (s, 0.6H, *endo* bridgehead- H), 2.68 (s, 0.6H, *endo* bridgehead- H), 2.47 (s, 0.4H, *exo* bridgehead- H), 2.46 – 2.39 (m, 0.6H, *endo* aliphatic- H), 1.90 (ddd, $J = 11.8, 9.2, 3.8$ Hz, 0.6H, *endo* aliphatic- H), 1.78 – 1.71 (m, 0.4H, *exo* aliphatic- H), 1.41 (dq, $J = 8.4, 2.0$ Hz, 0.6H, *endo* aliphatic- H), 1.32 – 1.21 (m, 1.4H, aliphatic- H), 1.14 – 1.03 (m, 0.8H, *exo* aliphatic- H), 0.53 (ddd, $J = 11.8, 4.5, 2.6$ Hz, 0.6H, *endo* aliphatic- H).

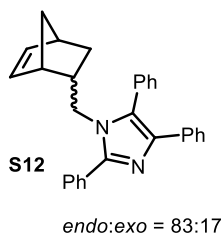
^{13}C NMR (101 MHz, Chloroform- d) δ 139.15, 137.48, 135.65, 135.62, 135.53, 132.74, 132.24, 130.88, 130.67, 130.64, 130.56, 130.52, 130.51, 130.49, 130.47, 130.45, 129.38, 129.35, 129.22, 125.01, 124.52, 52.66, 51.75, 49.52, 44.65, 44.06, 43.95, 42.36, 41.74, 39.66, 39.22, 34.87, 34.84, 30.80, 30.22.

HRMS (ESI): Calcd for $\text{C}_{24}\text{H}_{25}\text{N}_2^+$ (M^+): 341.2012, found: 341.2027.

A full assignment of ^1H NMR and ^{13}C NMR can be found in Figure S54 and Figure S55, based on its COSY, NOESY, and HSQC.



Benzaldehyde (1.06 g, 10.0 mmol), benzil (2.10 g, 10.0 mmol), and 5-norbornene-2-methylamine (1.24 g, 10.1 mmol) were combined with ammonium acetate (0.77 g, 10.0 mmol) and L-proline (172 mg, 1.5 mmol) in methanol and stirred at 60 °C for 12 hours. After cooling to room temperature, the solvent was removed under reduced pressure. The residue was dissolved in chloroform, washed with H₂O, dried with MgSO₄, filtered, and concentrated under reduced pressure. The crude product was further purified on silica gel chromatography (hexane/ethyl acetate = 5:1) to afford the product as a white solid (35% yield).



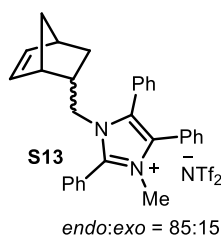
S12: White solid. R_f = 0.30 (hexane/ethyl acetate = 5:1).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.73 – 7.66 (m, 2H, aryl-*H*), 7.57 – 7.40 (m, 10H, aryl-*H*), 7.23 – 7.10 (m, 3H, aryl-*H*), 5.86 (dd, J = 5.7, 2.9 Hz, 0.17H, *exo* vinyl-*H*), 5.81 (dd, J = 5.8, 3.1 Hz, 0.83H, *endo* vinyl-*H*), 5.77 (dd, J = 5.7, 3.2 Hz, 0.17H, *exo* vinyl-*H*), 4.73 (dd, J = 5.8, 2.8 Hz, 0.83H, *endo* vinyl-*H*), 4.10 (dd, J = 14.3, 6.2 Hz, 0.17H, *exo* CH₂N), 3.88 (dd, J = 14.3, 10.1 Hz, 0.17H, *exo* CH₂N), 3.78 (dd, J = 14.3, 5.3 Hz, 0.83H, *endo* CH₂N), 3.68 (dd, J = 14.3, 9.1 Hz, 0.83H, *endo* CH₂N), 2.62 – 2.48 (m, 1H, bridgehead-*H*), 2.38 – 2.28 (m, 0.83H, *endo* bridgehead-*H*), 2.14 (dd, J = 3.2, 1.5 Hz, 0.17H, *exo* bridgehead-*H*), 2.02 – 1.81 (m, 1.66H, aliphatic-*H*), 1.45 (ddd, J = 11.7, 9.4, 3.9 Hz, 0.83H, *endo* aliphatic-*H*), 1.32 – 1.22 (m, 0.17H, *exo* aliphatic-*H*), 1.18 (dd, J = 8.4, 2.2 Hz, 0.83H, *endo* aliphatic-*H*), 0.97 – 0.89 (m, 1H, aliphatic-*H*), 0.89 – 0.82 (m, 0.17H, *exo* aliphatic-*H*), 0.75 (dt, J = 11.8, 3.8 Hz, 0.17H, *exo* aliphatic-*H*), 0.49 – 0.43 (m, 0.17H, *exo* aliphatic-*H*), 0.22 – 0.13 (m, 0.83H, *endo* aliphatic-*H*).

¹³C NMR (101 MHz, Chloroform-*d*) δ 148.00, 137.97, 137.88, 134.63, 131.77, 131.61, 131.59, 131.07, 131.01, 129.74, 129.36, 129.28, 129.06, 129.04, 128.72, 128.64, 128.61, 128.52, 128.46, 127.99, 126.98, 126.84, 126.20, 49.41, 48.61, 43.91, 42.02, 40.13, 30.25.

HRMS (ESI): Calcd for C₂₉H₂₇N₂⁺ (M+H⁺): 403.2169, found: 403.2172.

S13 were synthesized from **S12** via general procedure B.



S13: White solid. R_f = 0.30 (hexane/ethyl acetate = 5:1).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.84 (dd, J = 5.4, 2.2 Hz, 2H, aryl-*H*), 7.72 (dd, J = 5.0, 1.9 Hz, 3H, aryl-*H*), 7.54 – 7.29 (m, 10H, aryl-*H*), 5.88 (dd, J = 5.7, 2.9 Hz, 0.15H, *exo* vinyl-*H*), 5.83 (dd, J = 5.8, 3.0 Hz, 1H, vinyl-*H*), 4.63 (dd, J = 5.8, 2.8 Hz, 0.85H, *endo* vinyl-*H*), 4.26 (dd, J = 14.5, 6.2 Hz, 0.15H, *exo* CH_2N), 4.02 (dd, J = 14.5, 10.1 Hz, 0.15H, *exo* CH_2N), 3.93 – 3.79 (m, 1.7H, *endo* CH_2N), 3.56 (d, J = 3.5 Hz, 3H, CH_3), 2.55 (d, J = 3.3 Hz, 1H, bridgehead-*H*), 2.42 (t, J = 2.7 Hz, 0.85H, *endo* bridgehead-*H*), 2.20 (d, J = 2.9 Hz, 0.15H, *exo* bridgehead-*H*), 1.93 (dd, J = 9.2, 4.7 Hz, 0.85H, *endo* aliphatic-*H*), 1.48 (ddd, J = 11.8, 9.4, 3.8 Hz, 0.85H, *endo* aliphatic-*H*), 1.22 (dq, J = 8.5, 2.1 Hz, 1.15H, aliphatic-*H*), 0.98 (dt, J = 8.6, 1.5 Hz, 1.15H, aliphatic-*H*), 0.75 (dt, J = 11.9, 3.8 Hz, 0.15H, *exo* aliphatic-*H*), 0.34 (d, J = 9.0 Hz, 1H, *exo* aliphatic-*H*), 0.13 (ddd, J = 11.9, 4.7, 2.6 Hz, 0.85H, *endo* aliphatic-*H*).

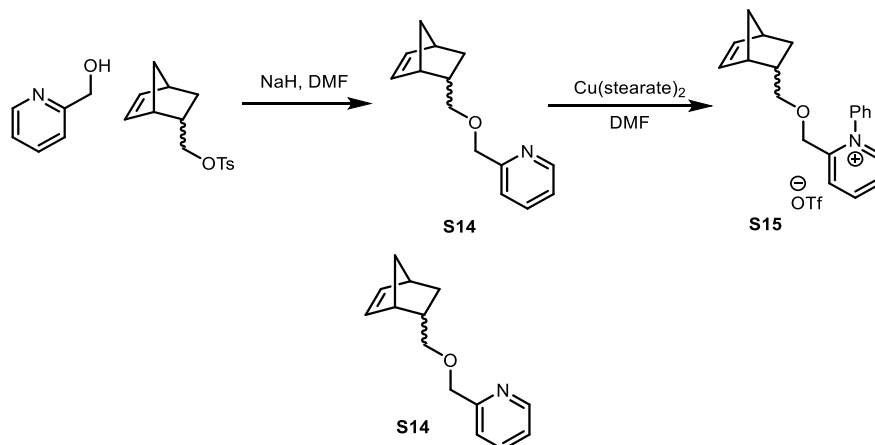
^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.45, 138.95, 132.98, 132.75, 131.84, 130.93, 130.87, 130.76, 130.67, 130.58, 130.26, 130.21, 130.13, 129.30, 129.27, 129.08, 125.74, 125.08, 122.09, 121.55, 50.54, 49.48, 43.92, 42.02, 39.19, 34.48, 30.43.

HRMS (ESI): Calcd for $\text{C}_{30}\text{H}_{29}\text{N}_2^+$ (M^+): 417.2325, found: 417.2319.

Under a nitrogen atmosphere, sodium hydride (520 mg, 60%, 13 mmol) was dispersed in anhydrous DMF (40 mL). Under stirring, pyridin-2-ylmethanol (1.14 mg, 12 mmol) was added in several portions. The reaction mixture was further stirred at room temperature for 2 hours. A DMF solution of (bicyclo[2.2.1]hept-5-en-2-yl)methyl 4-methylbenzenesulfonate (3.06 g, 11 mmol) was added dropwise to the reaction mixture. The mixture was further stirred at 80 °C for 16 hours. After cooling to room temperature, it was quenched and diluted by water. Then it was extracted by ethyl acetate, washed with water and brine, dried over MgSO_4 , and purified on silica gel chromatography (hexane/ethyl acetate = 5:1) to afford the product **S14** as a yellow liquid (40% yield).

A mixture of 2-(((bicyclo[2.2.1]hept-5-en-2-yl)methoxy)methyl)pyridine (215 mg, 1.0 mmol), Ph_2IOTf

(473 mg, 1.1 mmol) and copper(II) stearate (32 mg, 0.05 mmol) in anhydrous DMF (4 mL) was heated in 100 °C for 16 hours at an argon atmosphere. After cooling to room temperature, the reaction mixture was diluted by water. Then it was extracted by ethyl acetate, washed with water and brine, dried over MgSO₄, and purified on silica gel chromatography (dichloromethane/acetone = 3:1) to afford the product **S15** as a yellow solid (35% yield).

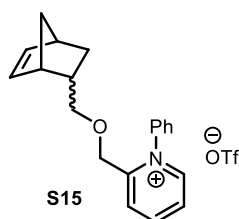


S14: Yellowish liquid. R_f = 0.55 (hexane/ethyl acetate = 1:1).

¹H NMR (400 MHz, Chloroform-*d*) δ 8.54 (s, 1H, aryl-*H*), 7.76 – 7.63 (m, 1H, aryl-*H*), 7.51 – 7.41 (m, 1H, aryl-*H*), 7.22 – 7.13 (m, 1H, aryl-*H*), 6.16 – 6.09 (m, 1H, vinyl-*H*), 6.07 (dt, J = 3.2, 1.7 Hz, 0.5H, *exo* vinyl-*H*), 5.91 (dd, J = 5.7, 2.8 Hz, 0.5H, *endo* vinyl-*H*), 4.65 (s, 1H, O-CH₂-py), 4.61 (s, 0.5H, O-CH₂-py), 4.59 (s, 0.5H, O-CH₂-py), 3.66 – 3.58 (m, 0.5H, O-CH₂), 3.50 – 3.42 (m, 0.5H, O-CH₂), 3.33 – 3.25 (m, 0.5H, O-CH₂), 3.19 – 3.11 (m, 0.5H, O-CH₂), 2.97 (s, 0.5H, bridgehead-*H*), 2.81 (s, 1.5H, bridgehead-*H*), 2.49 – 2.40 (m, 1.5H, aliphatic-*H*), 1.81 (dtdd, J = 17.3, 8.6, 4.0, 2.4 Hz, 1H, aliphatic-*H*), 1.48 – 1.10 (m, 3.5H, aliphatic-*H*), 0.52 (ddd, J = 11.6, 4.5, 2.4 Hz, 0.5H, *endo* aliphatic-*H*).

¹³C NMR (101 MHz, Chloroform-*d*) δ 148.97, 137.25, 136.71, 136.65, 136.60, 136.56, 132.39, 122.28, 122.23, 121.29, 121.24, 75.70, 74.80, 73.93, 73.83, 49.43, 45.02, 44.00, 43.73, 42.19, 41.55, 38.92, 38.83, 29.70, 29.11.

HRMS (ESI): Calcd for C₁₄H₁₈NO⁺ (M+H⁺): 216.1383, found: 216.1415.



S15: Off-white solid. R_f = 0.10 (dichloromethane/acetone = 2:1).

^1H NMR (500 MHz, Chloroform- d) δ 8.70 – 8.61 (m, 2H, aryl- H), 8.29 (ddd, J = 7.7, 5.4, 1.5 Hz, 1H, aryl- H), 8.17 – 8.09 (m, 1H, aryl- H), 7.71 – 7.59 (m, 5H, aryl- H), 6.06 (dtd, J = 14.1, 5.7, 2.9 Hz, 1.5H, vinyl- H), 5.82 (dd, J = 5.8, 2.9 Hz, 0.5H, *endo* vinyl- H), 4.49 (d, J = 2.1 Hz, 1H, O- CH_2 -py), 4.42 (s, 1H, O- CH_2 -py), 3.50 (dd, J = 9.1, 6.3 Hz, 0.5H, O- CH_2), 3.37 (t, J = 9.0 Hz, 0.5H, O- CH_2), 3.17 (dd, J = 9.0, 6.6 Hz, 0.5H, O- CH_2), 3.08 (t, J = 9.0 Hz, 0.5H, O- CH_2), 2.85 (dq, J = 3.5, 1.7 Hz, 0.5H, bridgehead- H), 2.81 – 2.74 (m, 1H, bridgehead- H), 2.70 – 2.64 (m, 0.5H, bridgehead- H), 2.38 – 2.25 (m, 0.5H, aliphatic- H), 1.78 (ddd, J = 11.7, 9.2, 3.8 Hz, 0.5H, aliphatic- H), 1.64 (ddt, J = 8.7, 4.3, 2.5 Hz, 0.5H, aliphatic- H), 1.41 (dq, J = 8.3, 2.2 Hz, 0.5H, aliphatic- H), 1.30 (dt, J = 8.7, 2.0 Hz, 0.5H, aliphatic- H), 1.25 – 1.17 (m, 1.5H, aliphatic- H), 1.06 (dt, J = 11.7, 3.9 Hz, 0.5H, aliphatic- H), 0.44 (ddd, J = 11.7, 4.5, 2.6 Hz, 0.5H, *endo* aliphatic- H).

^{13}C NMR (126 MHz, Chloroform- d) δ 147.14, 147.12, 146.02, 145.99, 137.57, 136.85, 136.21, 131.99, 130.61, 127.59, 127.54, 127.02, 127.00, 125.27, 125.26, 76.60, 75.81, 67.96, 67.88, 49.34, 44.93, 43.81, 43.53, 42.06, 41.45, 38.63, 38.47, 29.43, 28.83.

HRMS (ESI): Calcd for $\text{C}_{14}\text{H}_{18}\text{NO}^+$ ($\text{M}+\text{H}^+$): 292.1726, found: 292.1726.

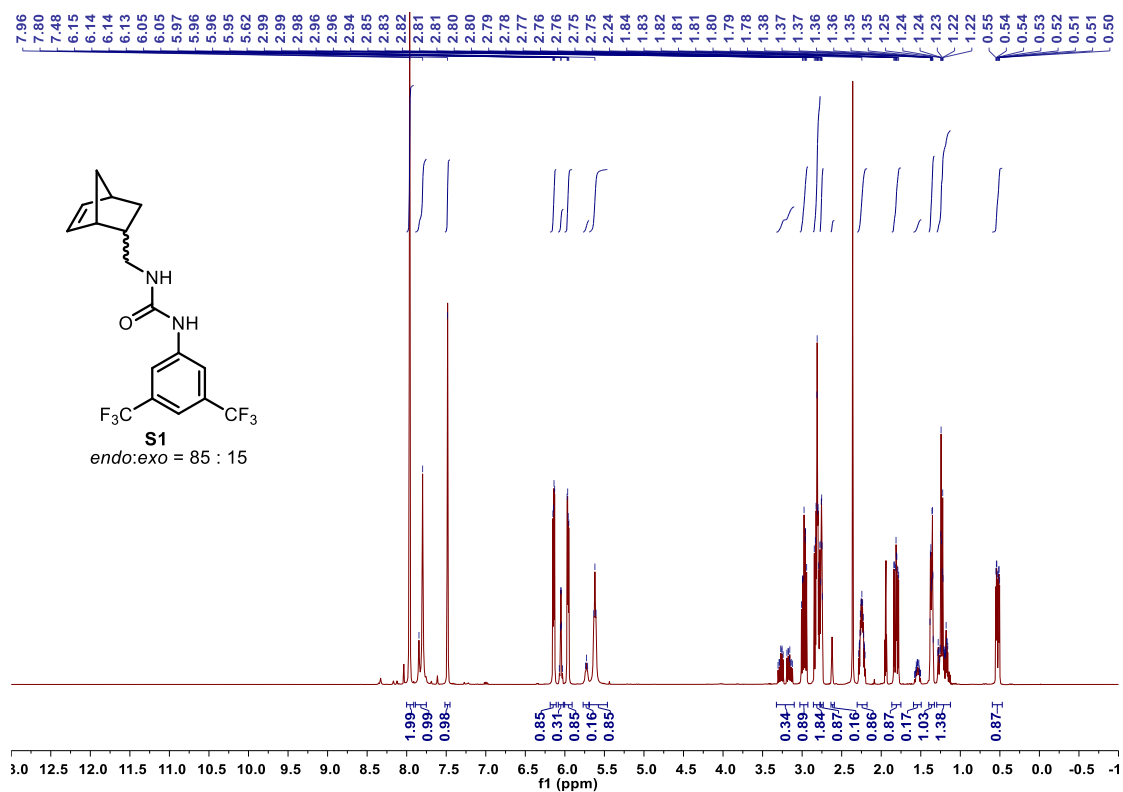


Figure S16. ¹H NMR spectrum of S1.

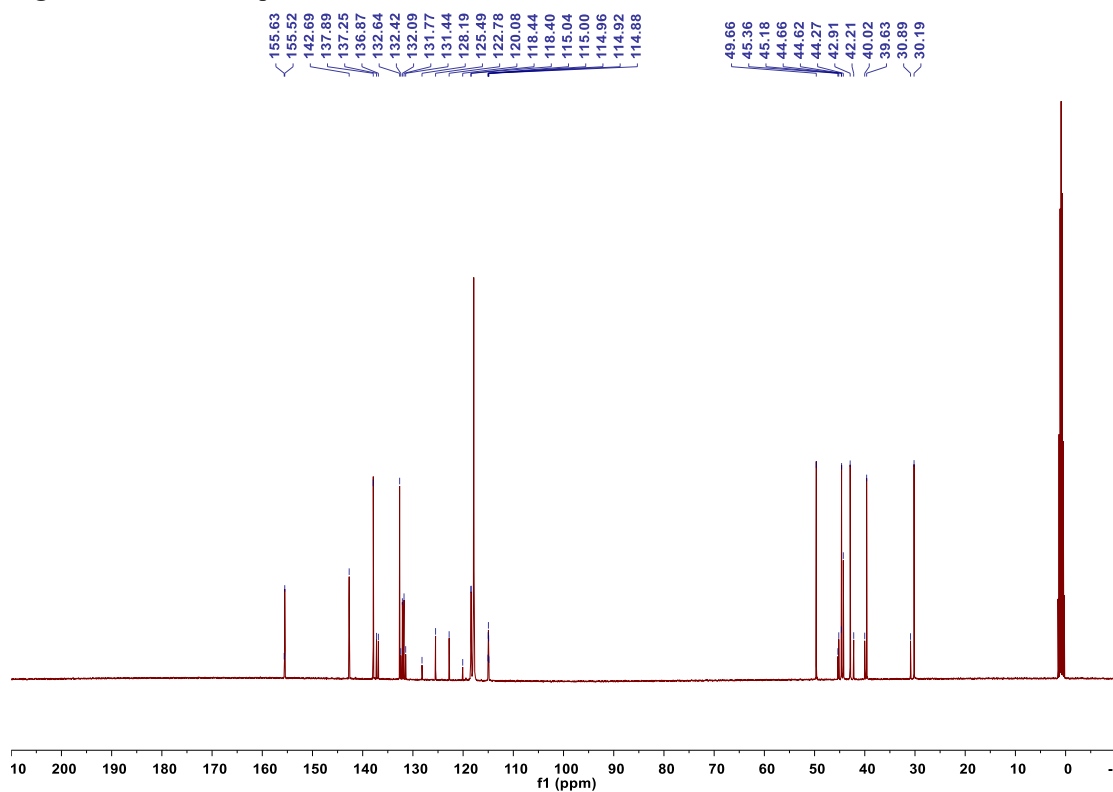


Figure S17. ¹³C NMR spectrum of S1.

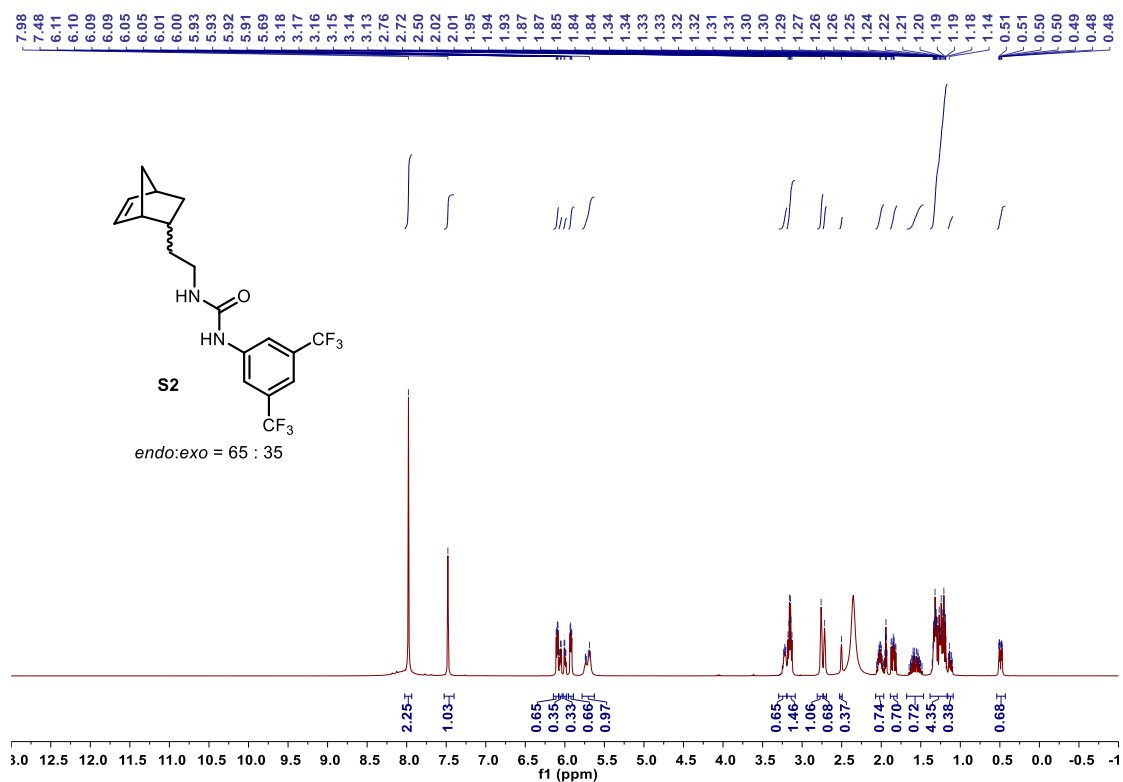


Figure S18. ¹H NMR spectrum of S2.

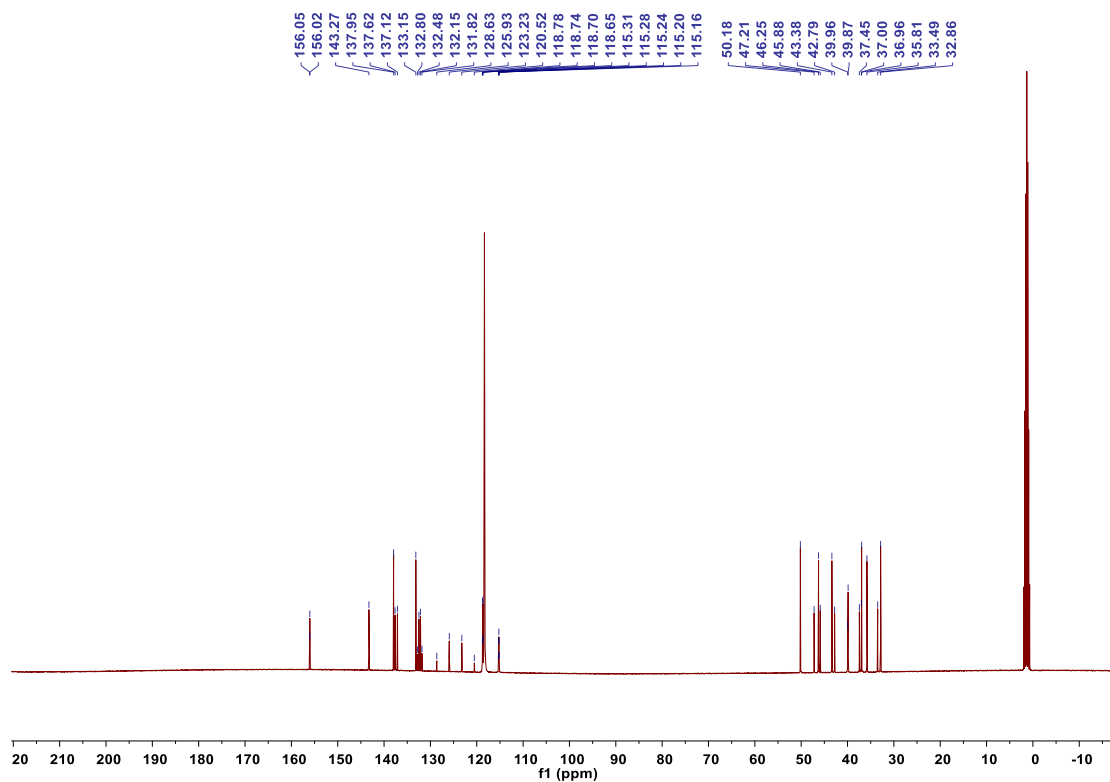


Figure S19. ¹³C NMR spectrum of S2.

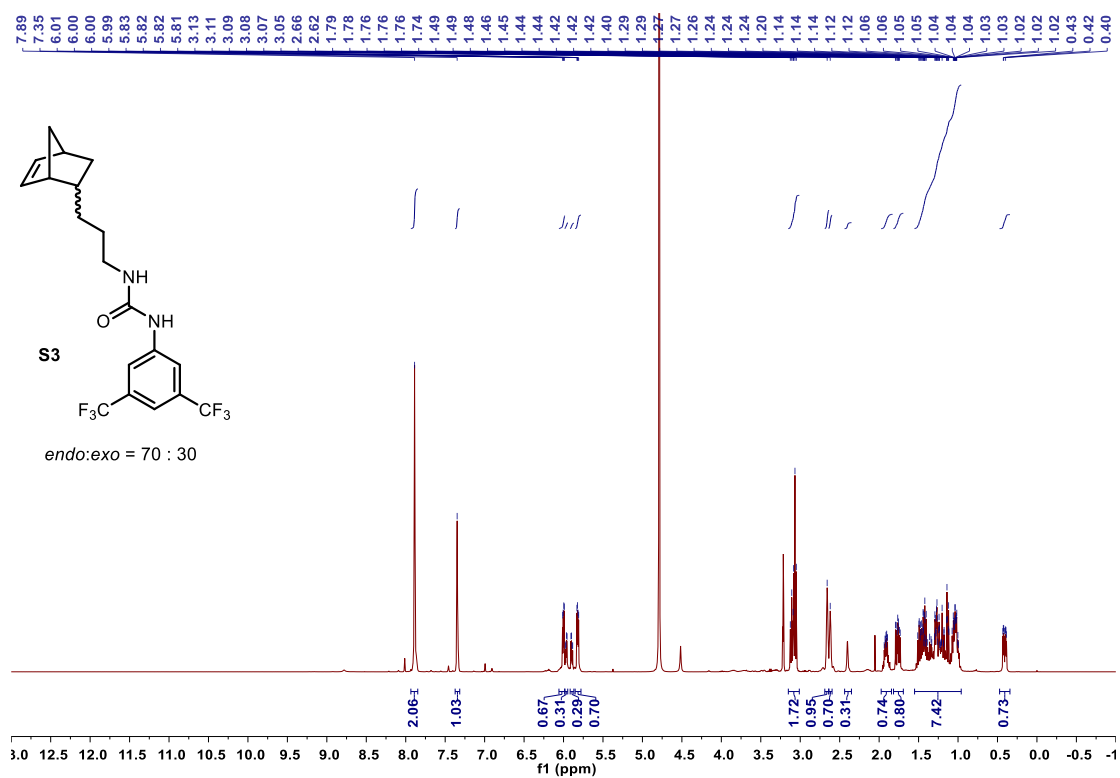


Figure S20. ^1H NMR spectrum of S3.

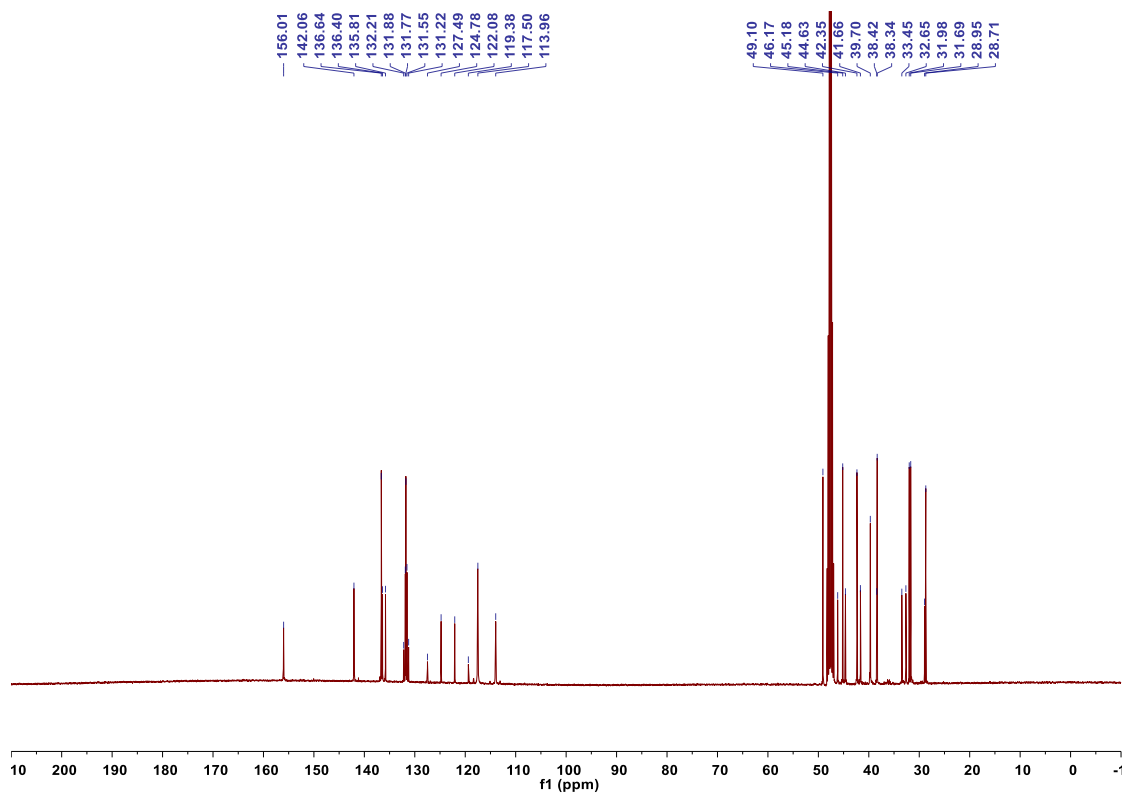


Figure S21. ^{13}C NMR spectrum of S3.

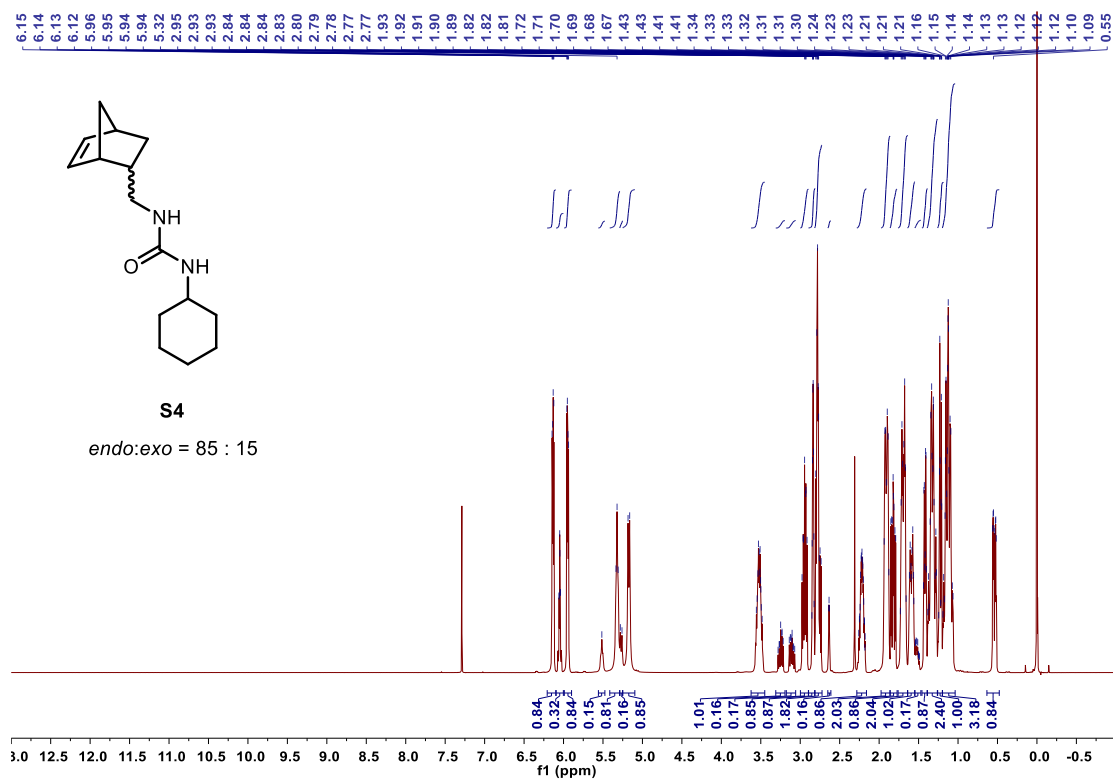


Figure S22. ¹H NMR spectrum of S4.

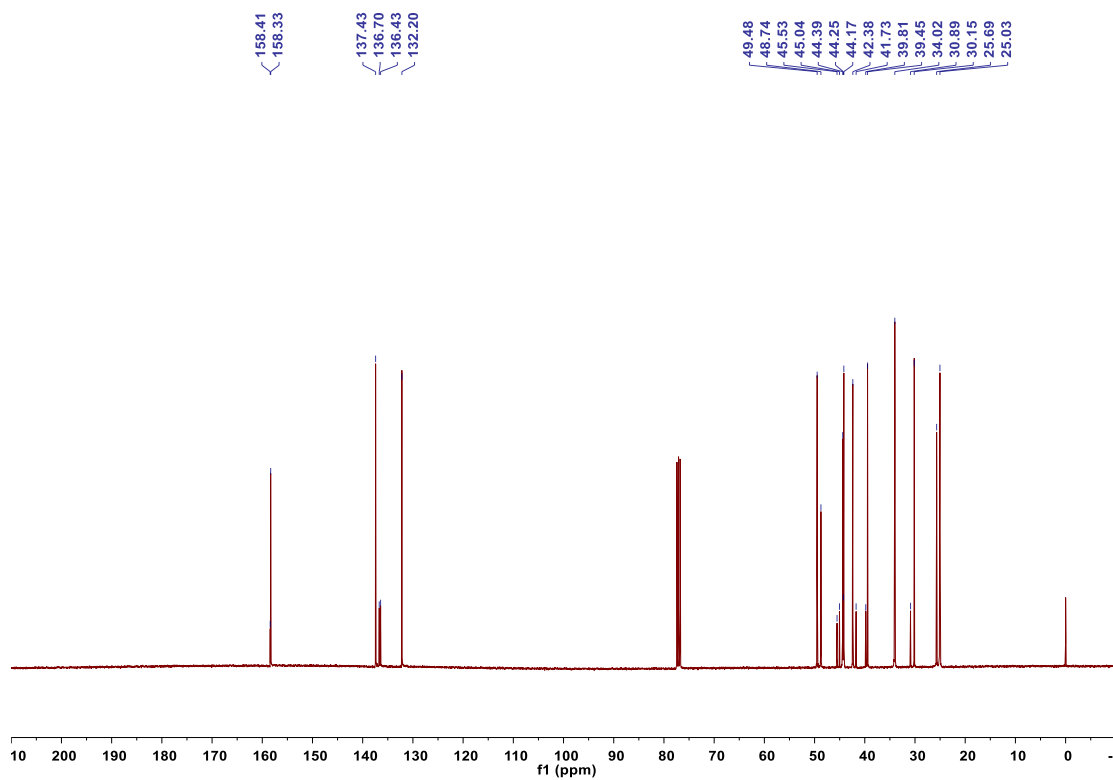


Figure S23. ¹³C NMR spectrum of S4.

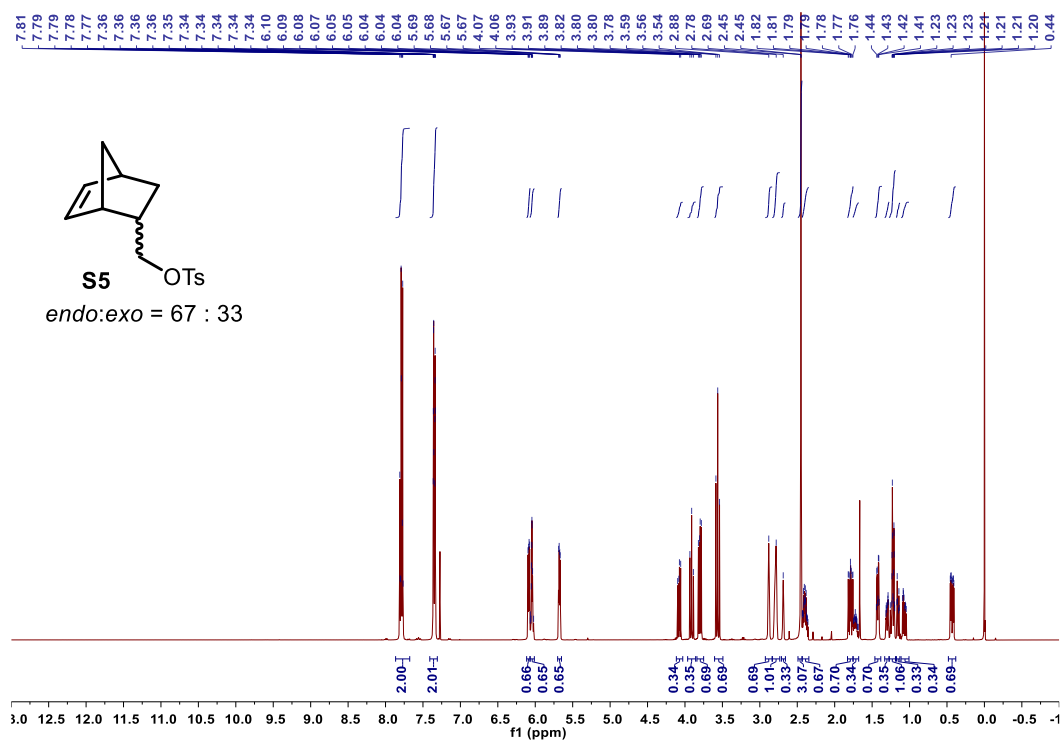


Figure S24. ^1H NMR spectrum of **S5**.

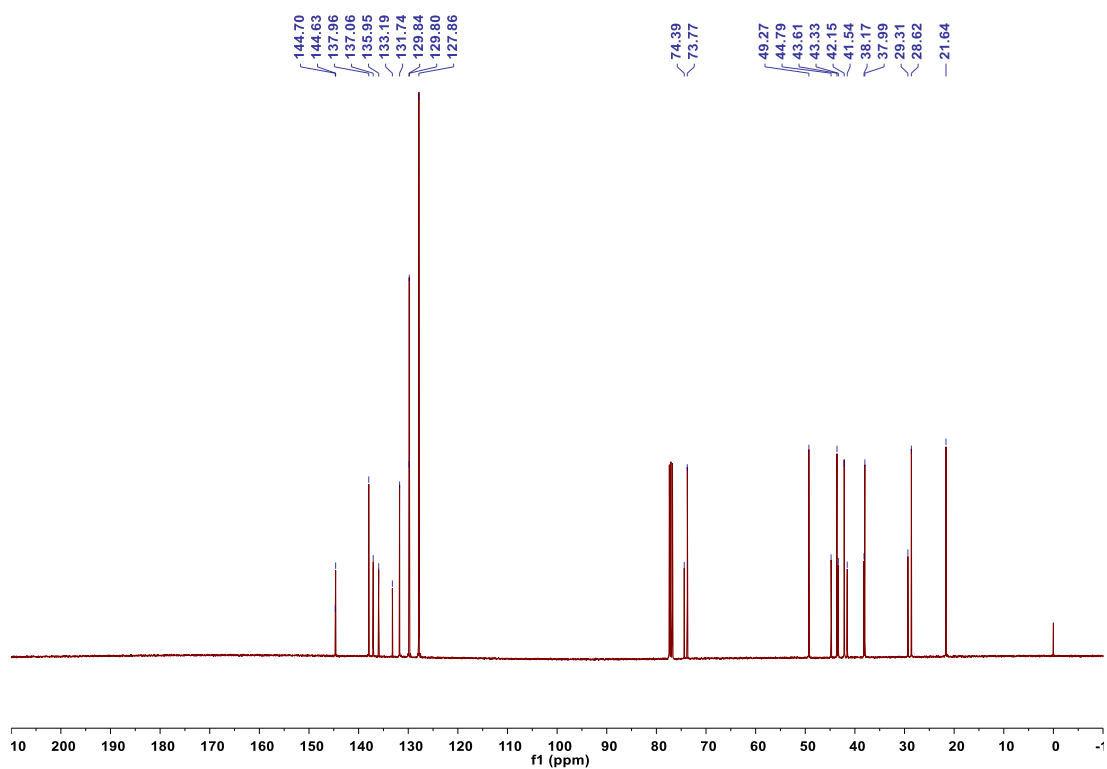


Figure S25. ^{13}C NMR spectrum of **S5**.

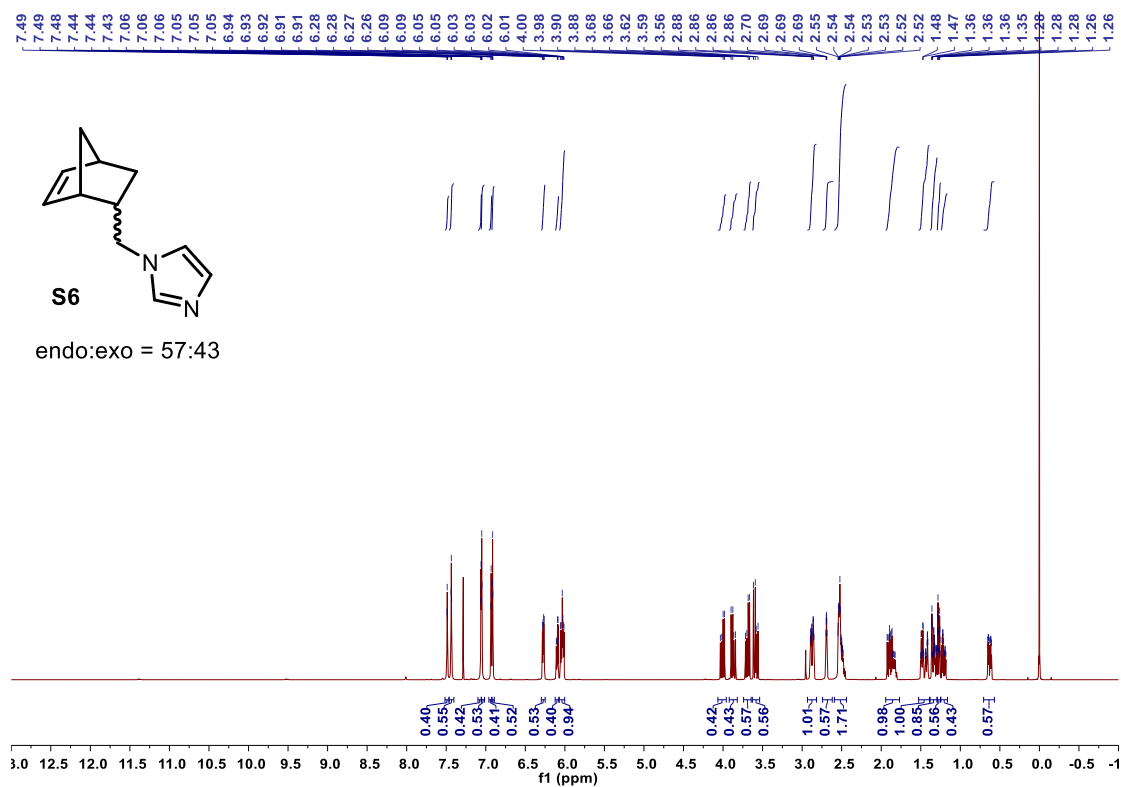


Figure S26. ¹H NMR spectrum of S6.

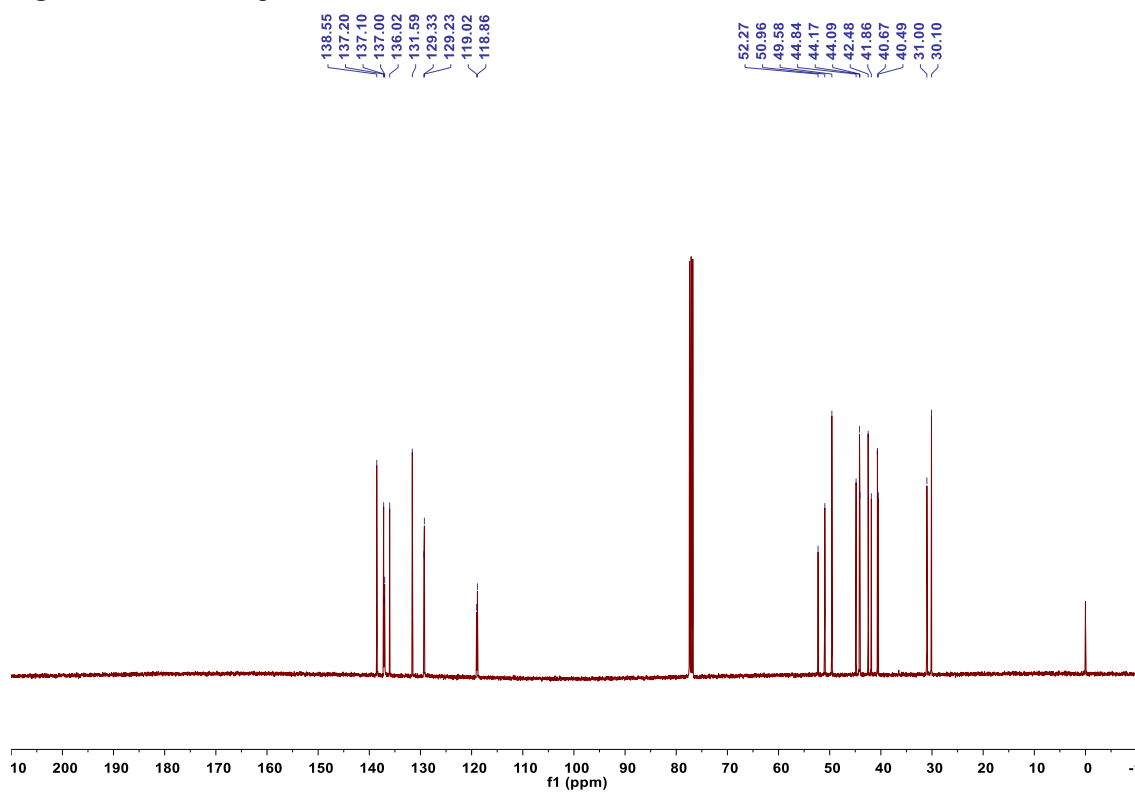


Figure S27. ¹³C NMR spectrum of S6.

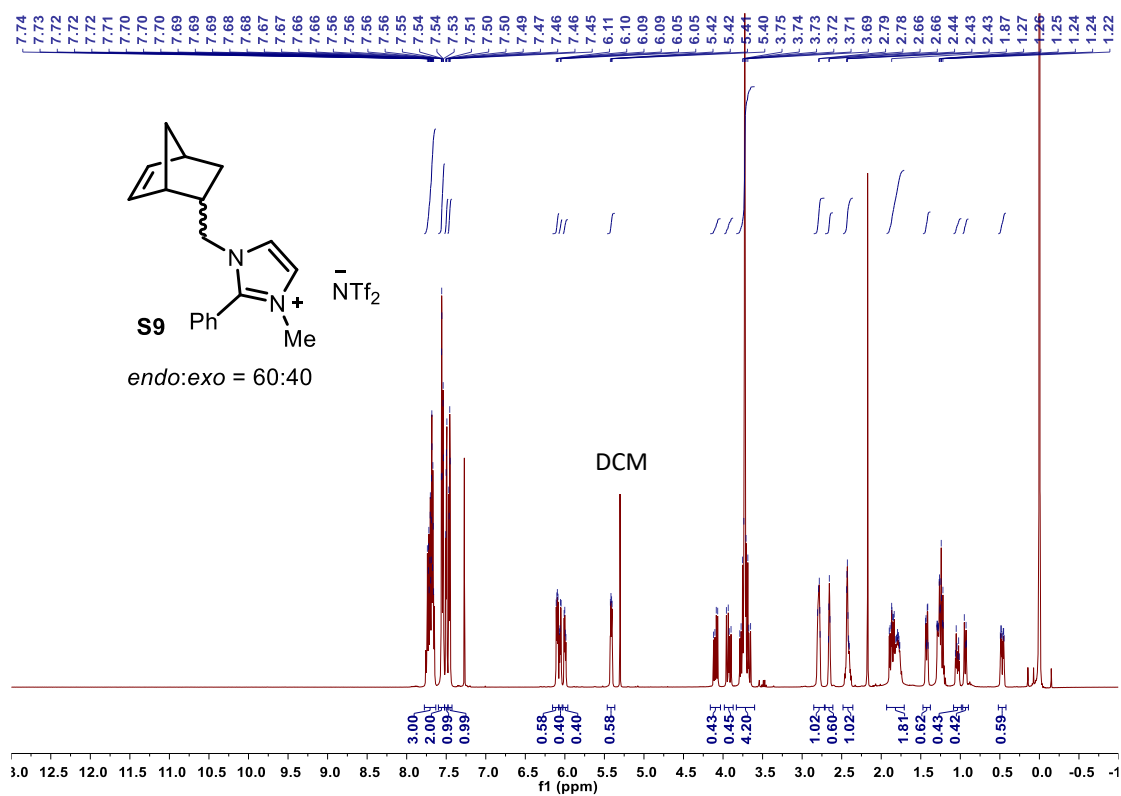


Figure S32. ^1H NMR spectrum of S9.

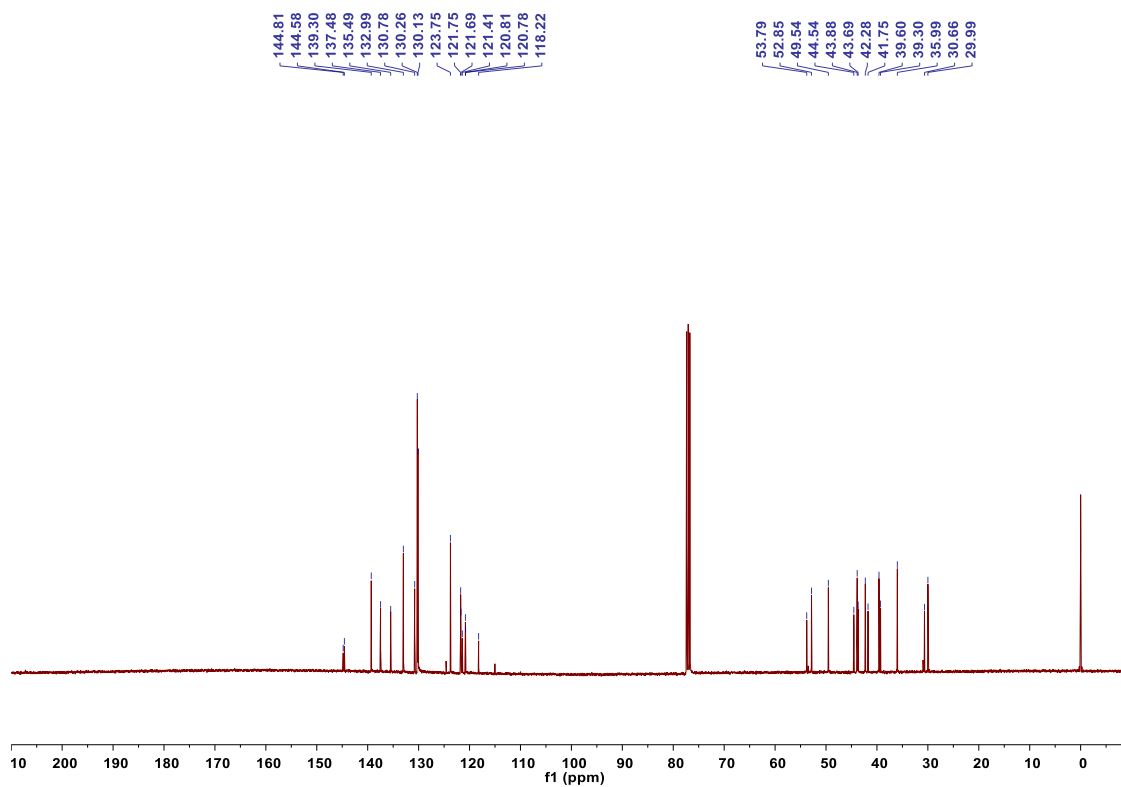


Figure S33. ^{13}C NMR spectrum of S9.

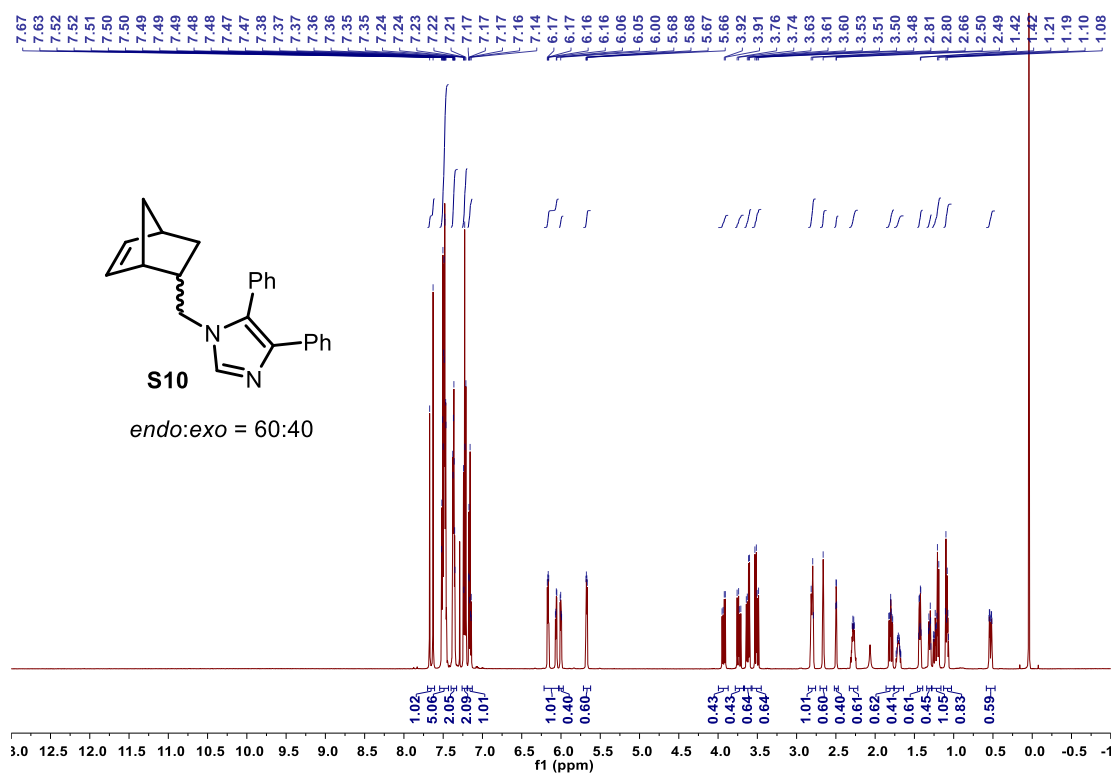


Figure S34. ¹H NMR spectrum of S10.

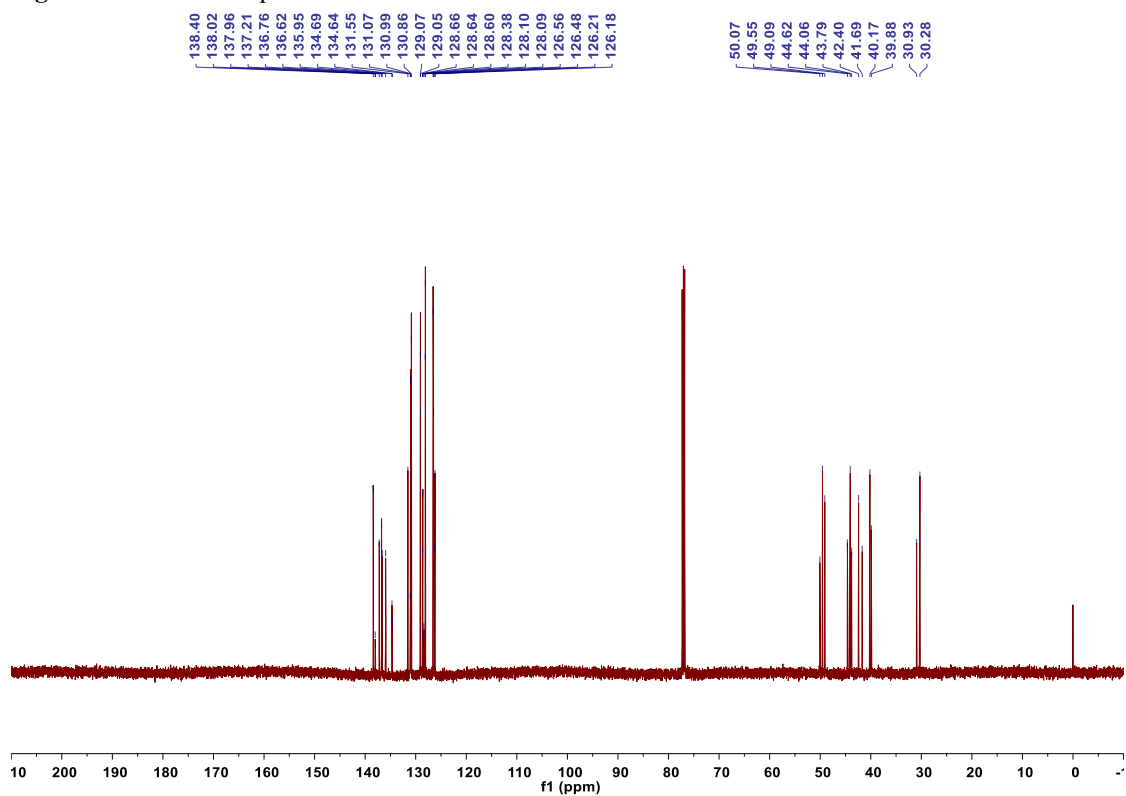


Figure S35. ¹³C NMR spectrum of S10.

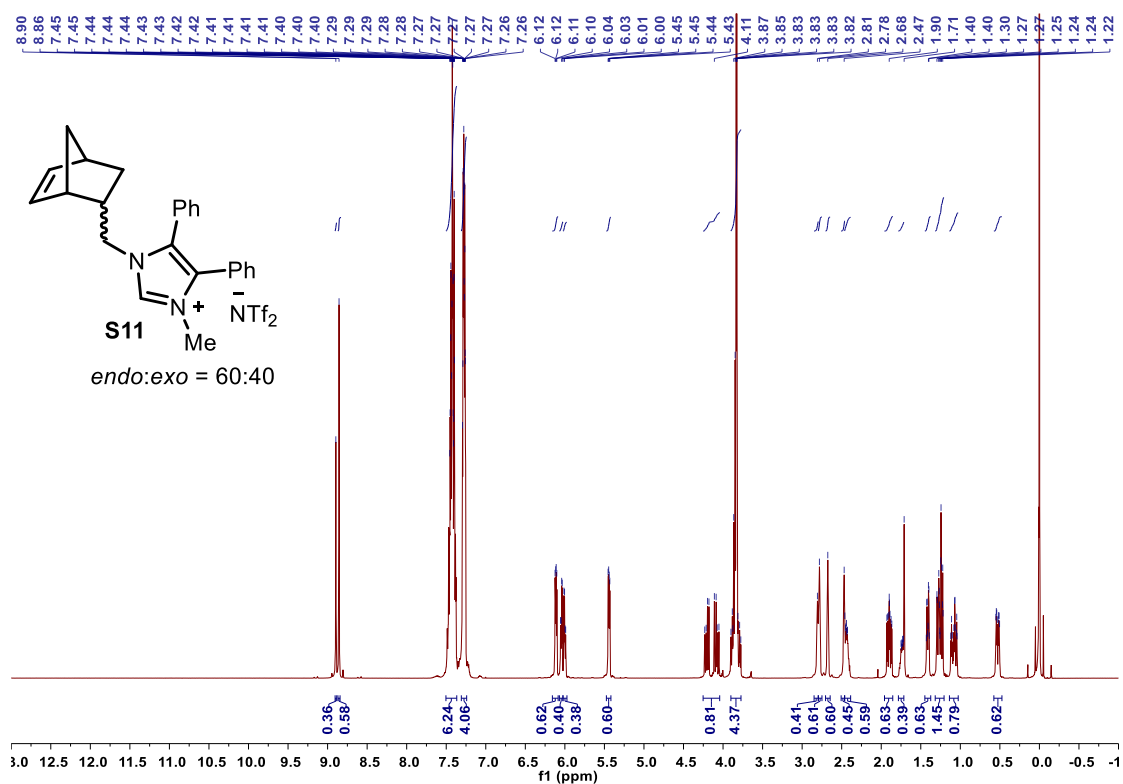


Figure S36. ¹H NMR spectrum of S11.

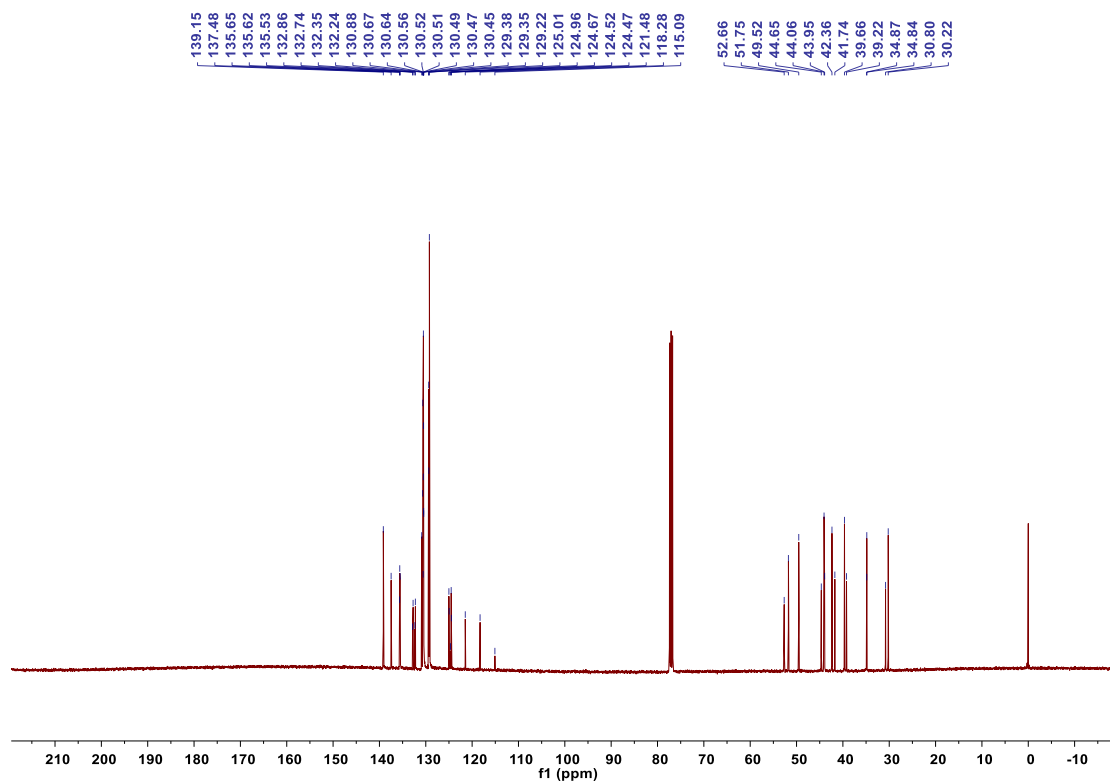


Figure S37. ¹³C NMR spectrum of S11.

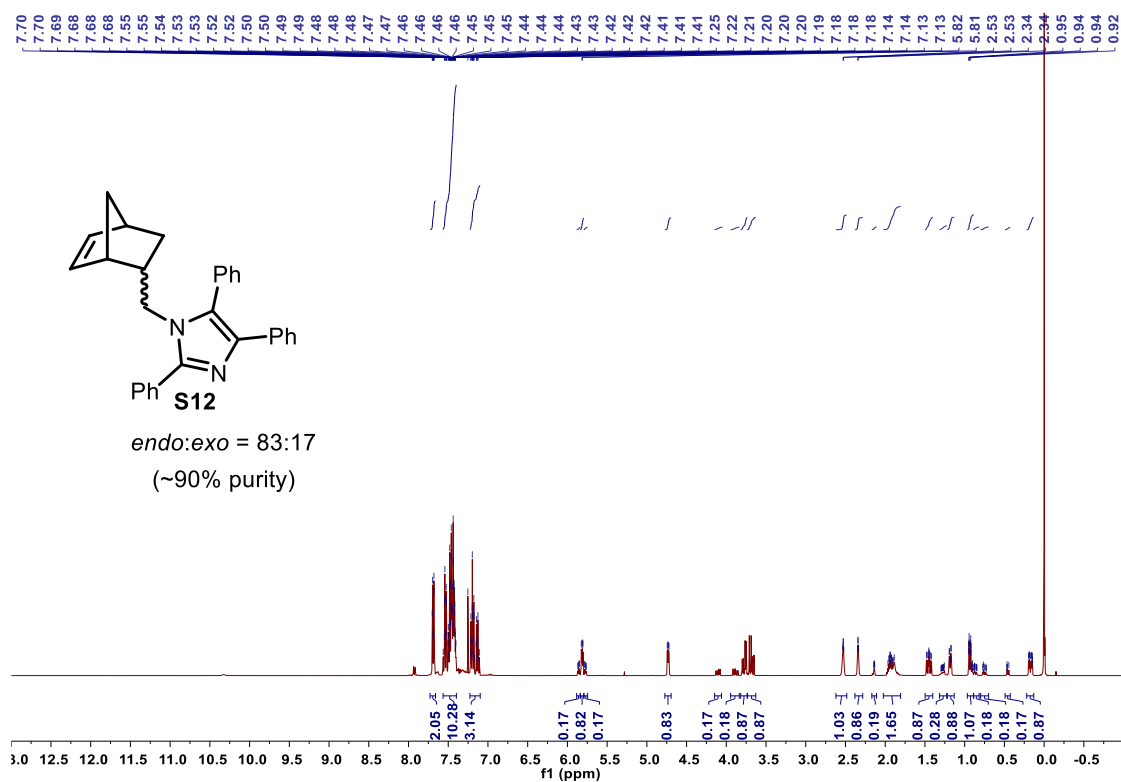


Figure S38. ¹H NMR spectrum of **S12**.

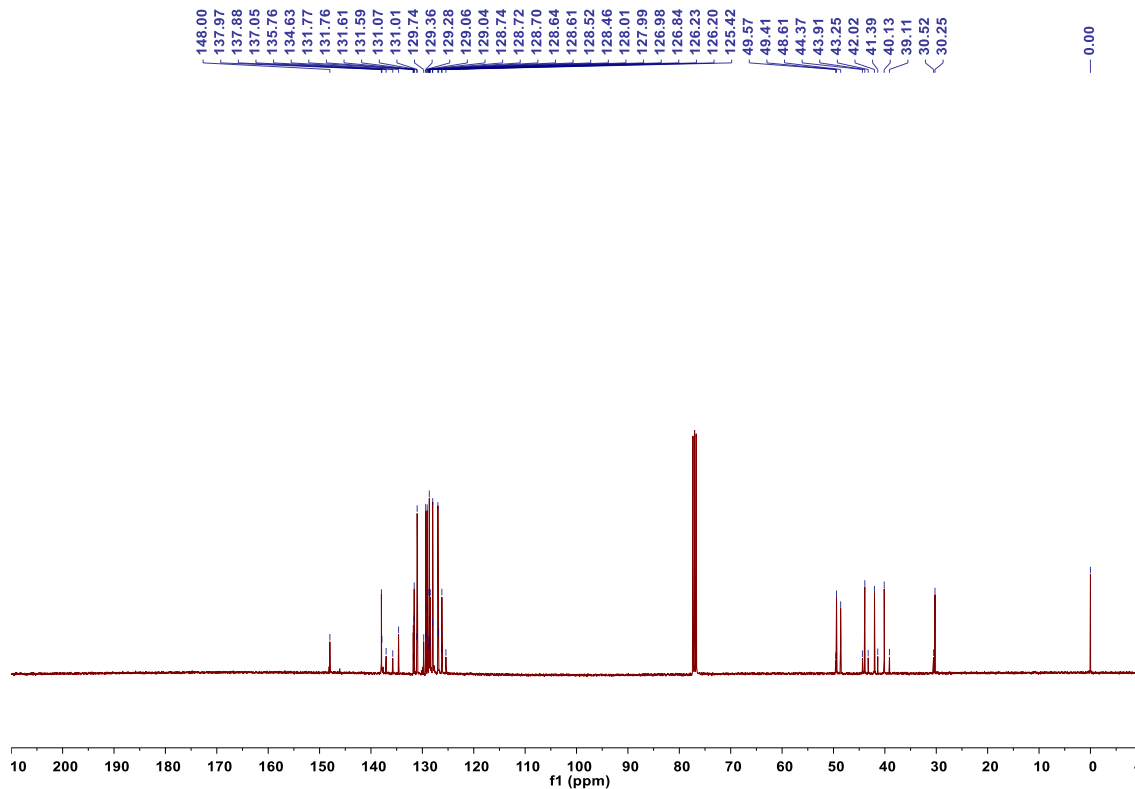


Figure S39. ¹³C NMR spectrum of **S12**.

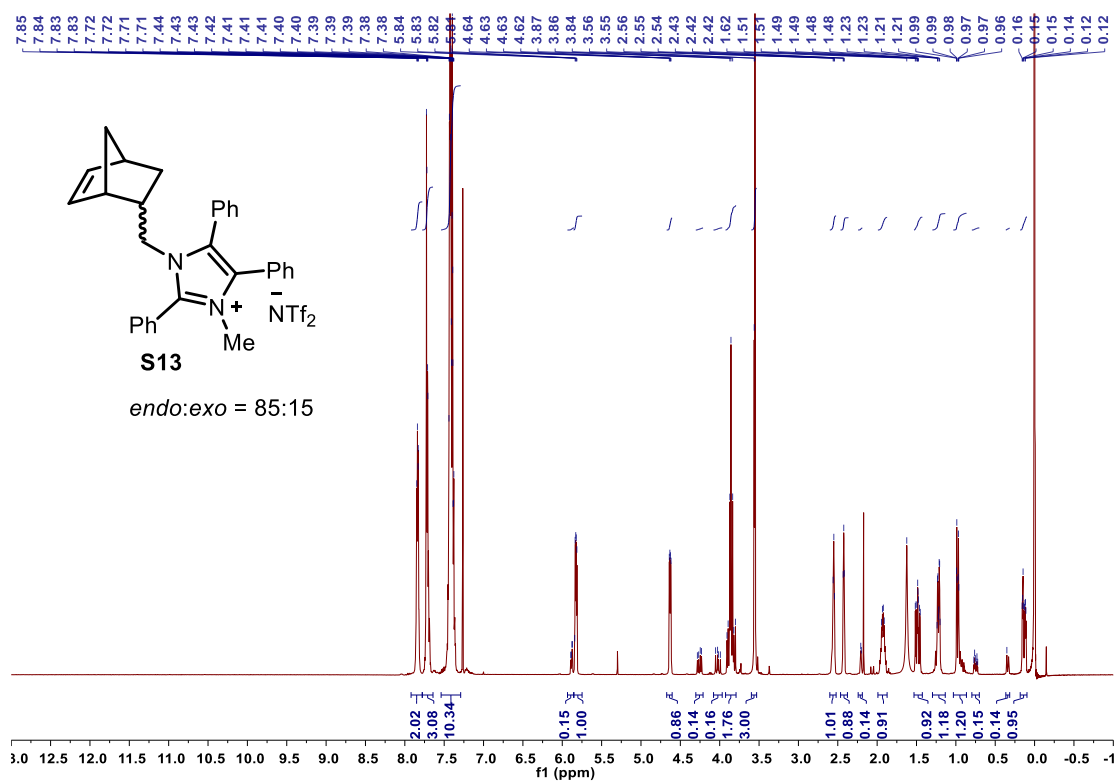


Figure S40. ¹H NMR spectrum of S13.

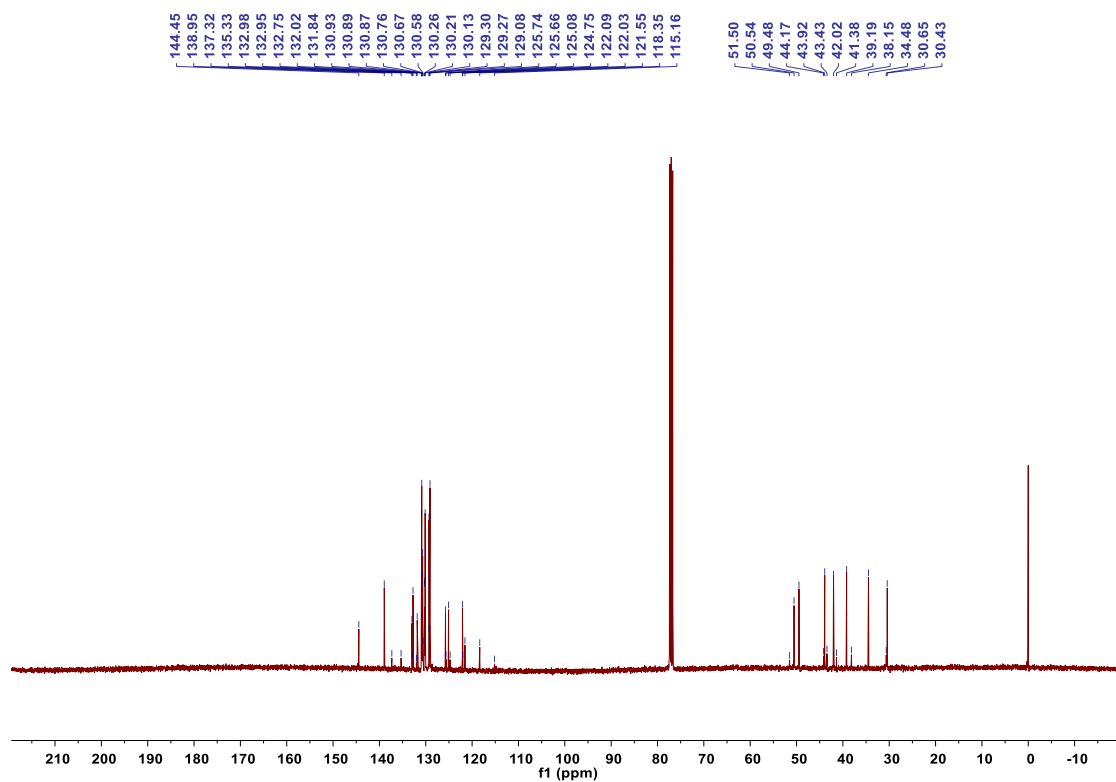


Figure S41. ¹³C NMR spectrum of S13.

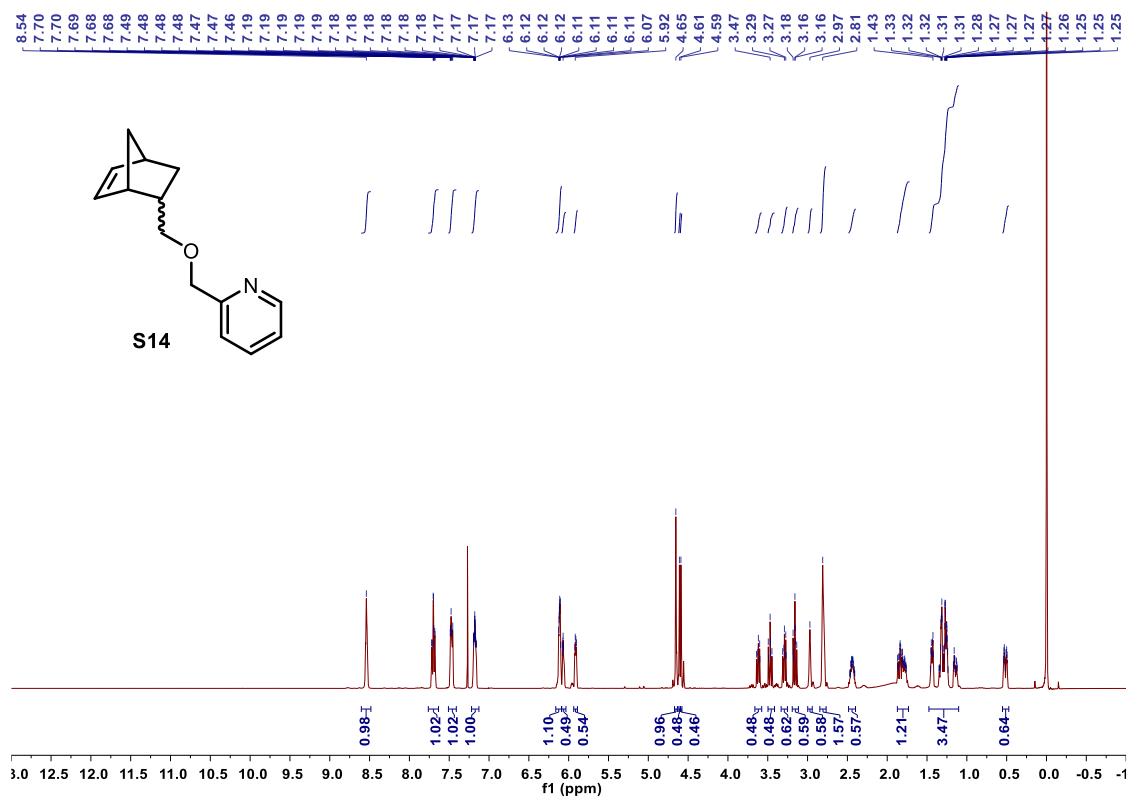


Figure S42. ¹H NMR spectrum of S14.

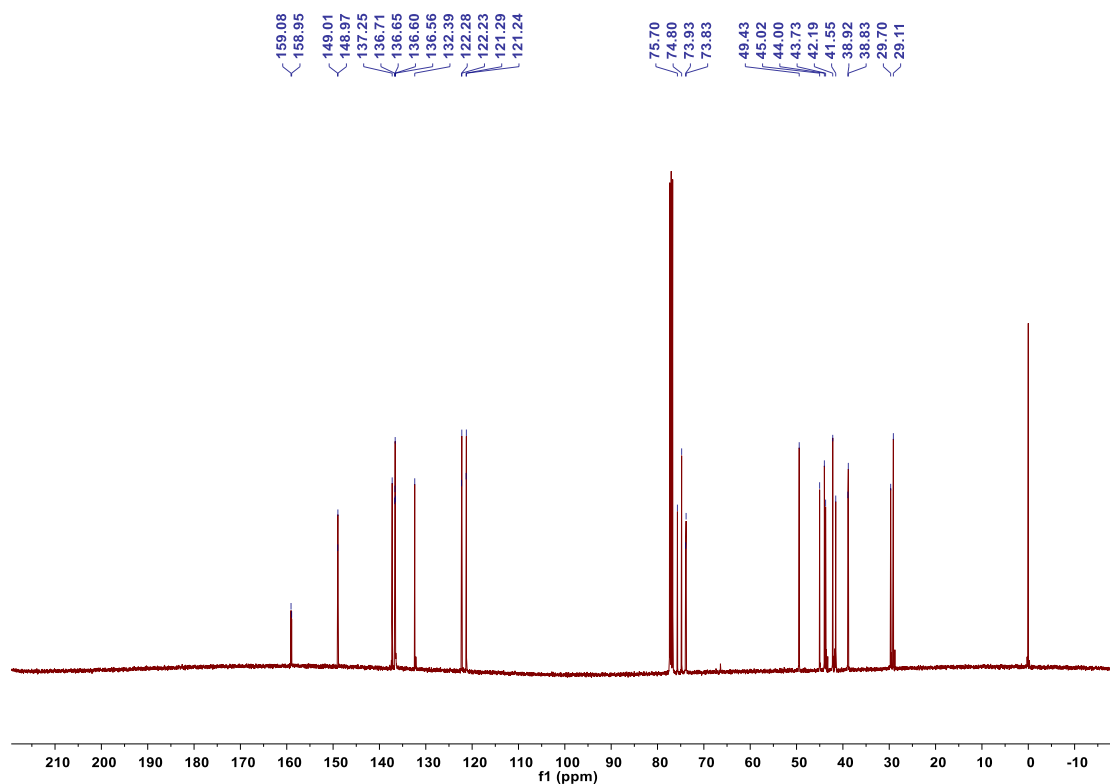


Figure S43. ¹³C NMR spectrum of S14.

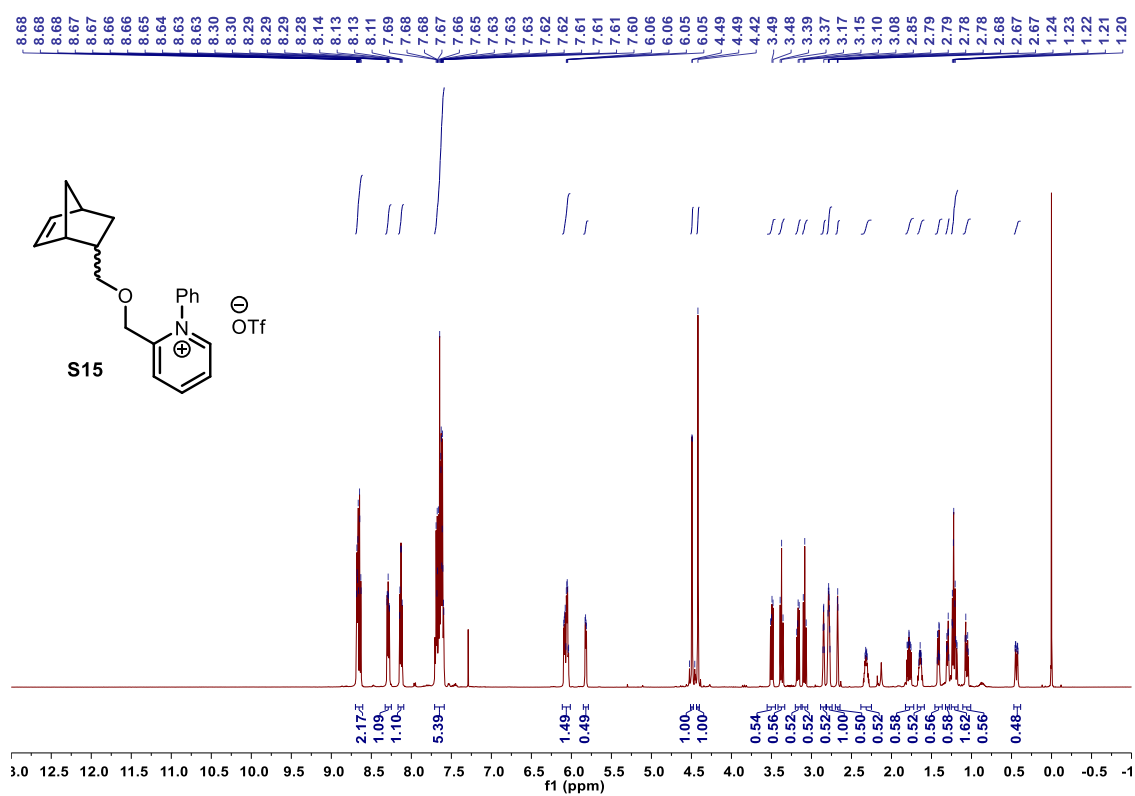


Figure S44. ¹H NMR spectrum of S15.

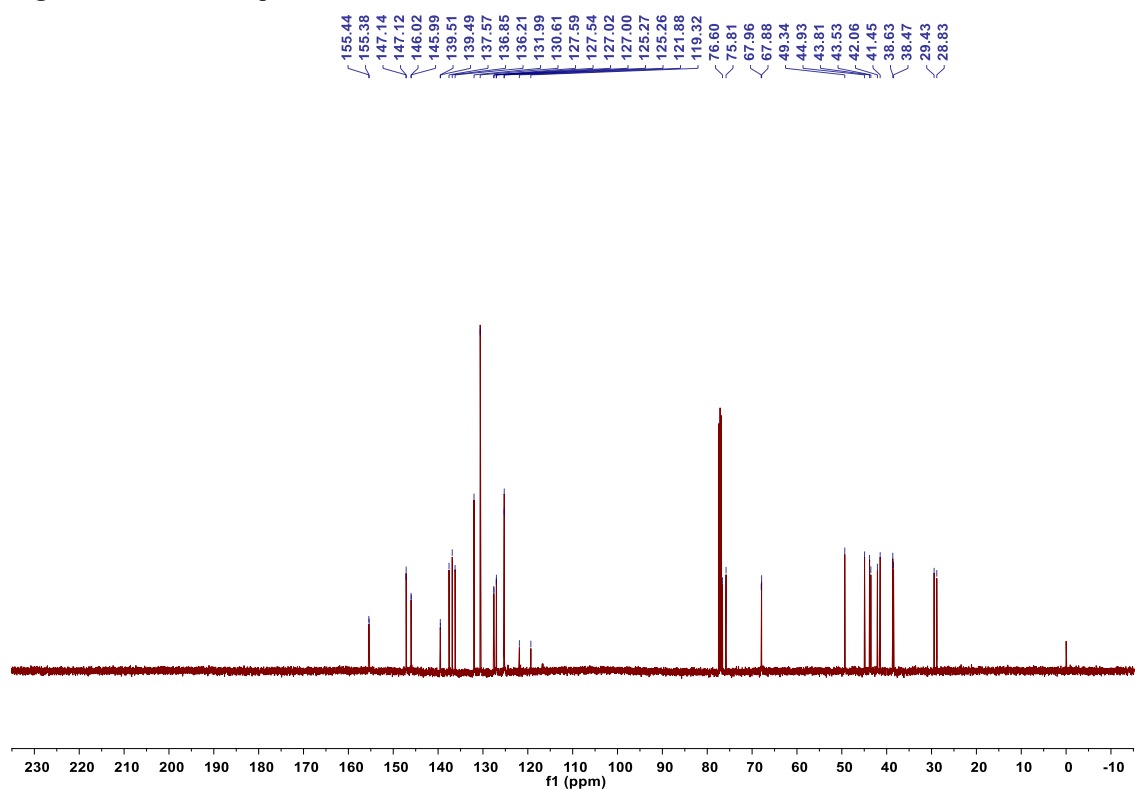


Figure S45. ¹³C NMR spectrum of S15.

Assignment of ^1H NMR and ^{13}C NMR

The ^1H and ^{13}C NMR spectra of compound **S6**, **S11**, **S2** were assigned based on the Correlation Spectroscopy (COSY), Nuclear Overhauser Effect Spectroscopy (NOESY), and Heteronuclear Single Quantum Coherence Spectroscopy (HSQC) spectra. In order to unambiguously assign the NMR spectra, pure *exo*-**S6** was also synthesized using *exo*-5-norbornene-2-methanol⁸. This allows us to assign every single proton and carbon for compound **S6**. The determination of *endo/exo* was based on (1) comparison with a pure *exo* sample and (2) the correlation signal on the NOESY spectrum.

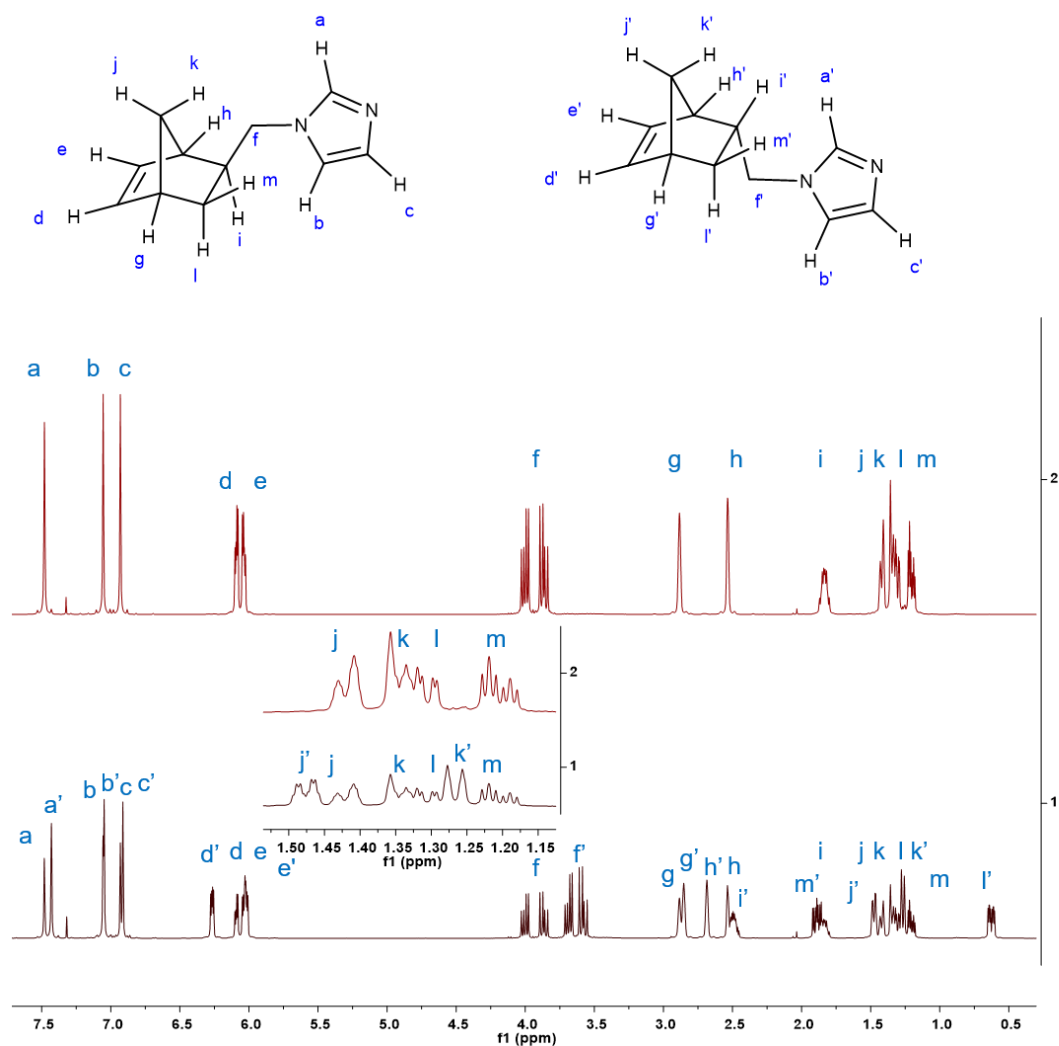


Figure S46. Assignment of ^1H NMR spectra of *exo*-**S6** (top) and **S6** (bottom, mixture of *endo* and *exo*).

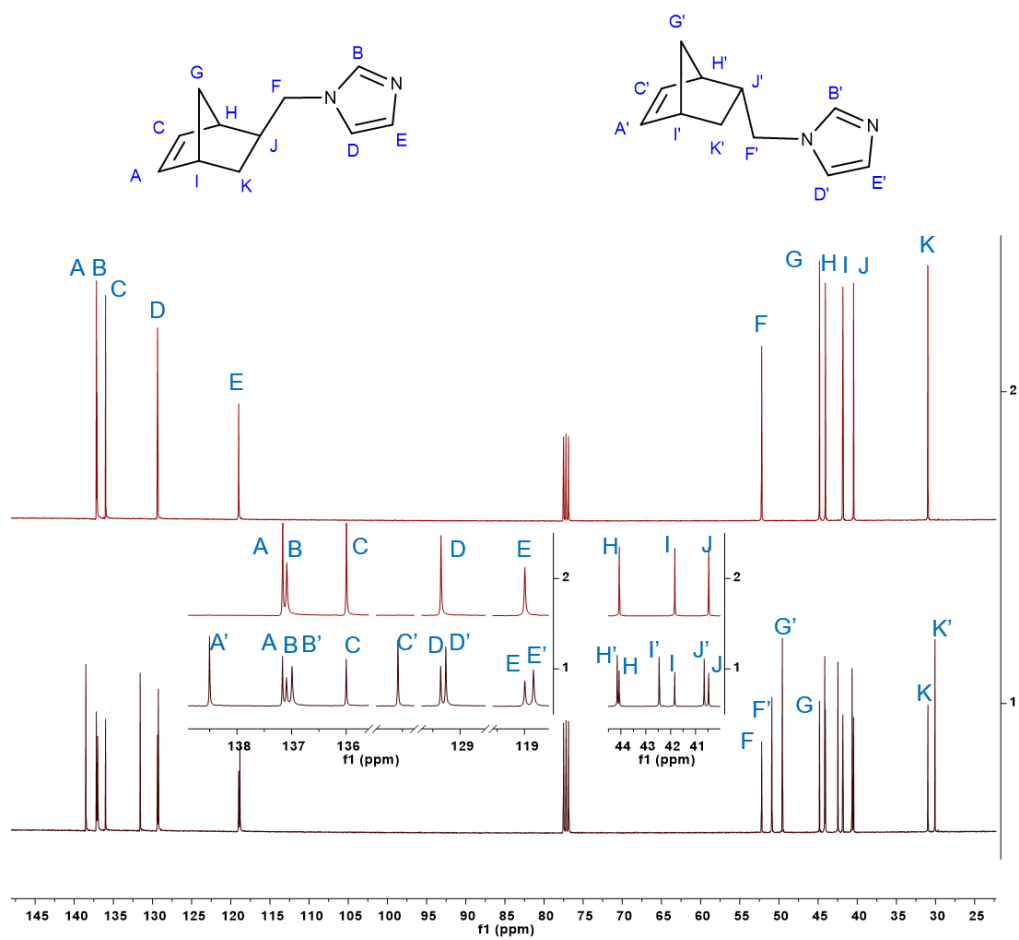


Figure S47. Assignment of ^{13}C NMR spectra of *exo*-S6 (top) and S6 (bottom, mixture of *endo* and *exo*).

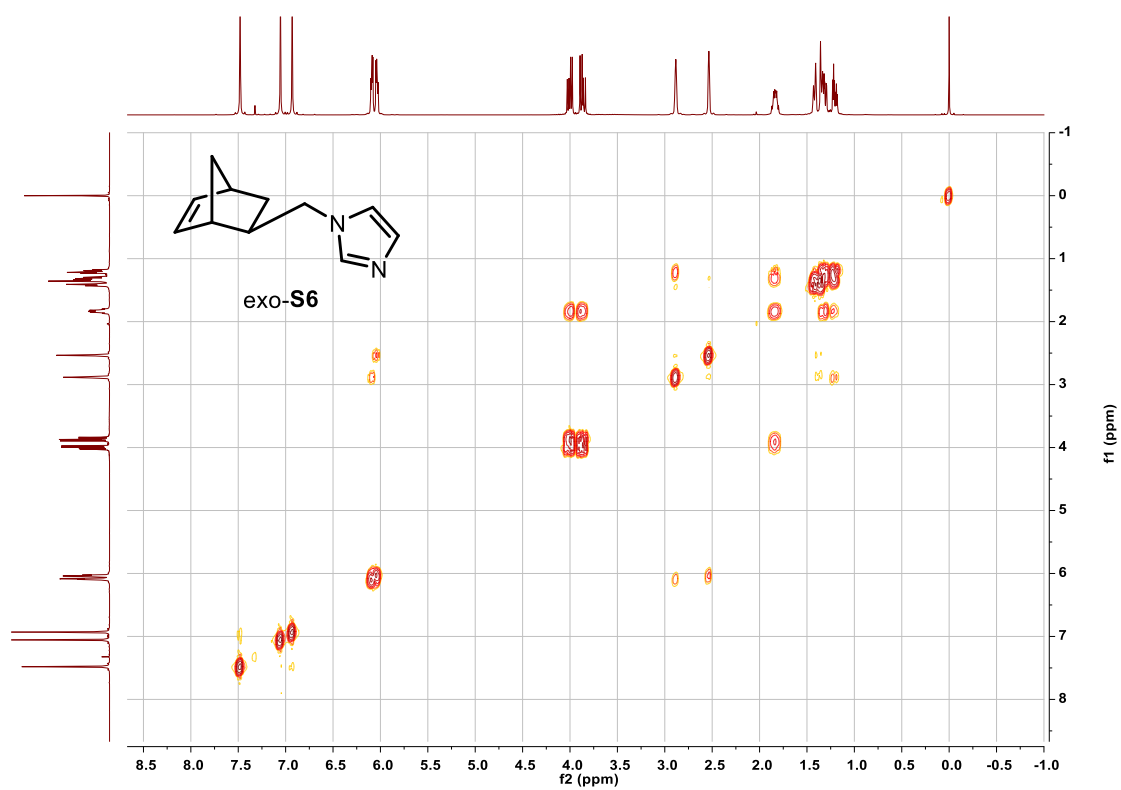


Figure S48. COSY spectrum of *exo*-S6.

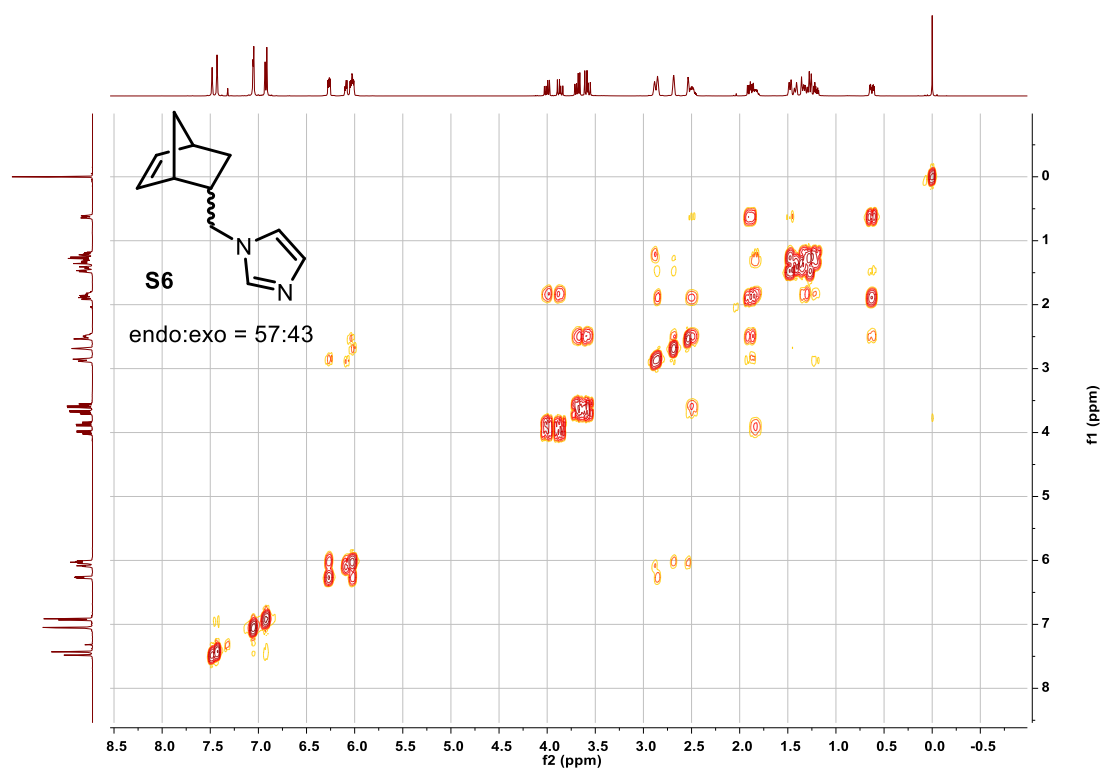


Figure S49. COSY spectrum of S6 (mixture of *endo* and *exo*).

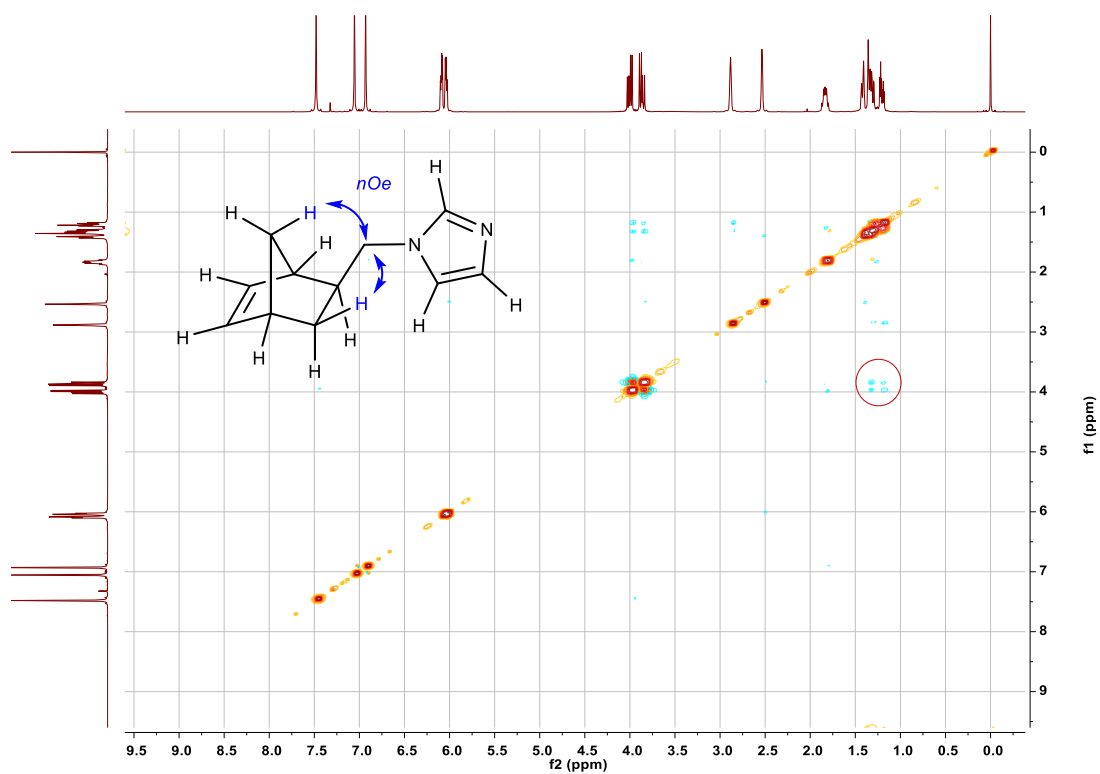


Figure S50. NOESY spectrum of *exo*-S6.

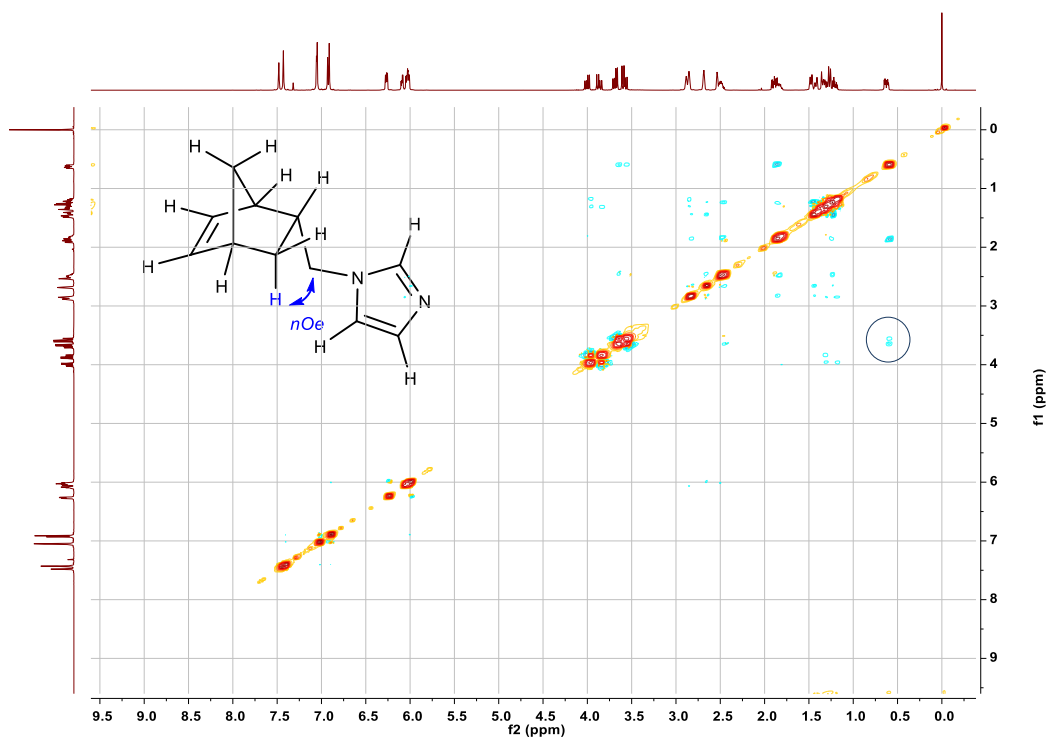


Figure S51. NOESY spectrum of S6 (mixture of *endo* and *exo*).

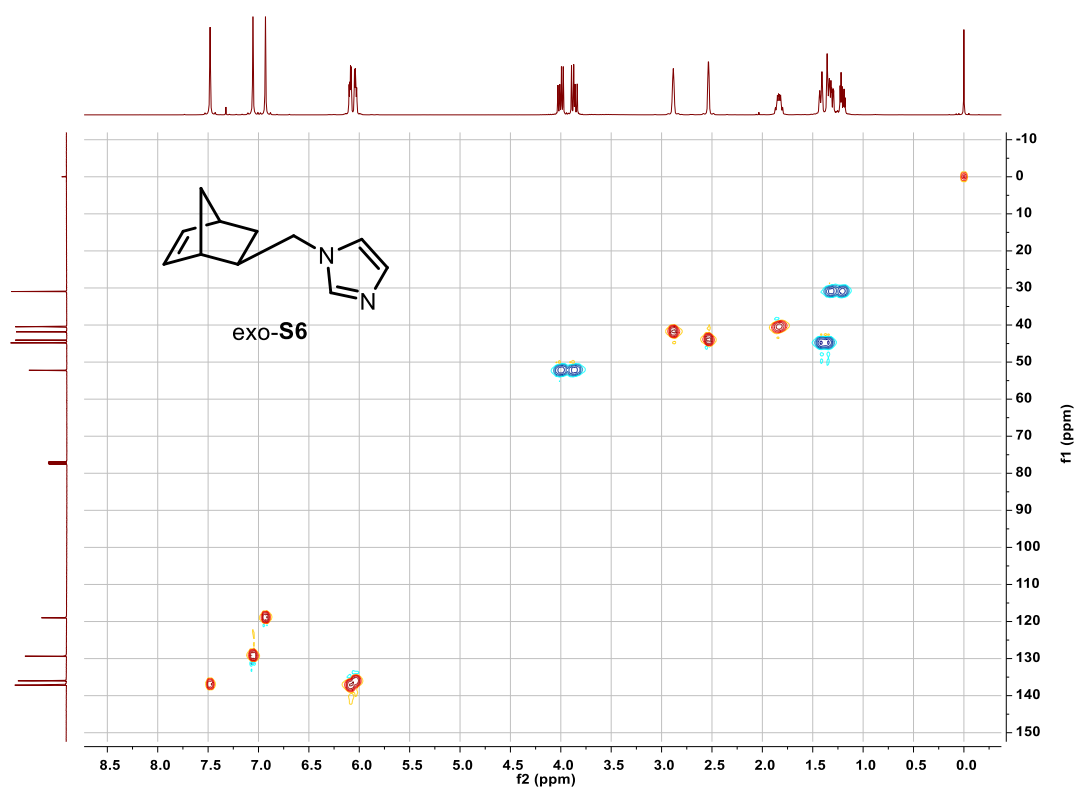


Figure S52. HSQC spectrum of *exo*-S6.

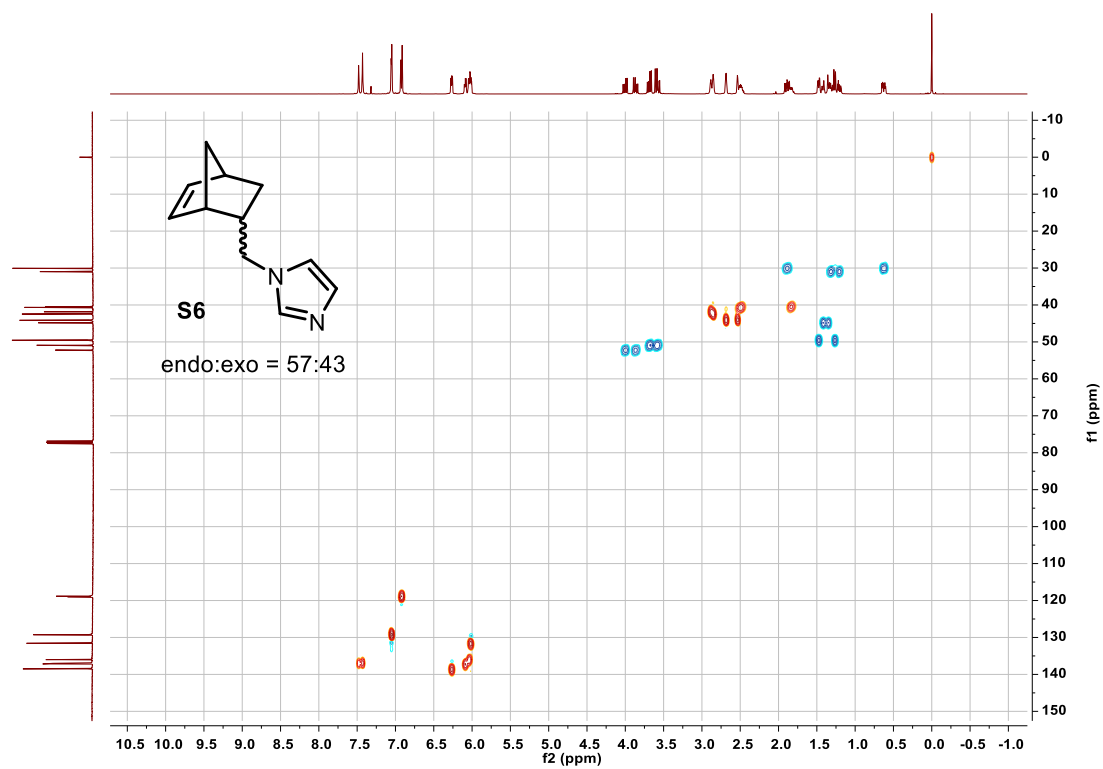


Figure S53. HSQC spectrum of S6 (mixture of *endo* and *exo*).

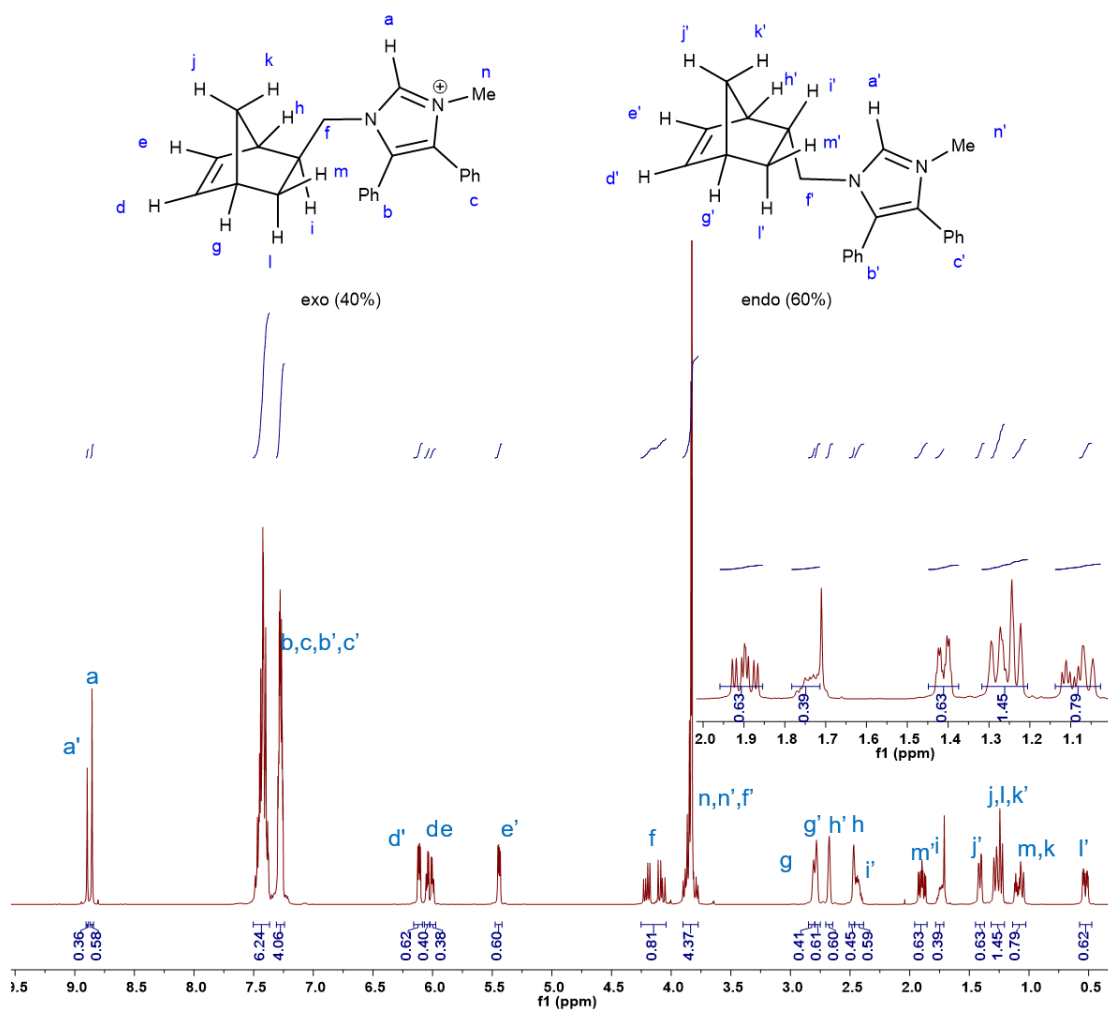


Figure S54. Assignment of ^1H NMR spectrum of S11 (*endo:exo* = 60:40).

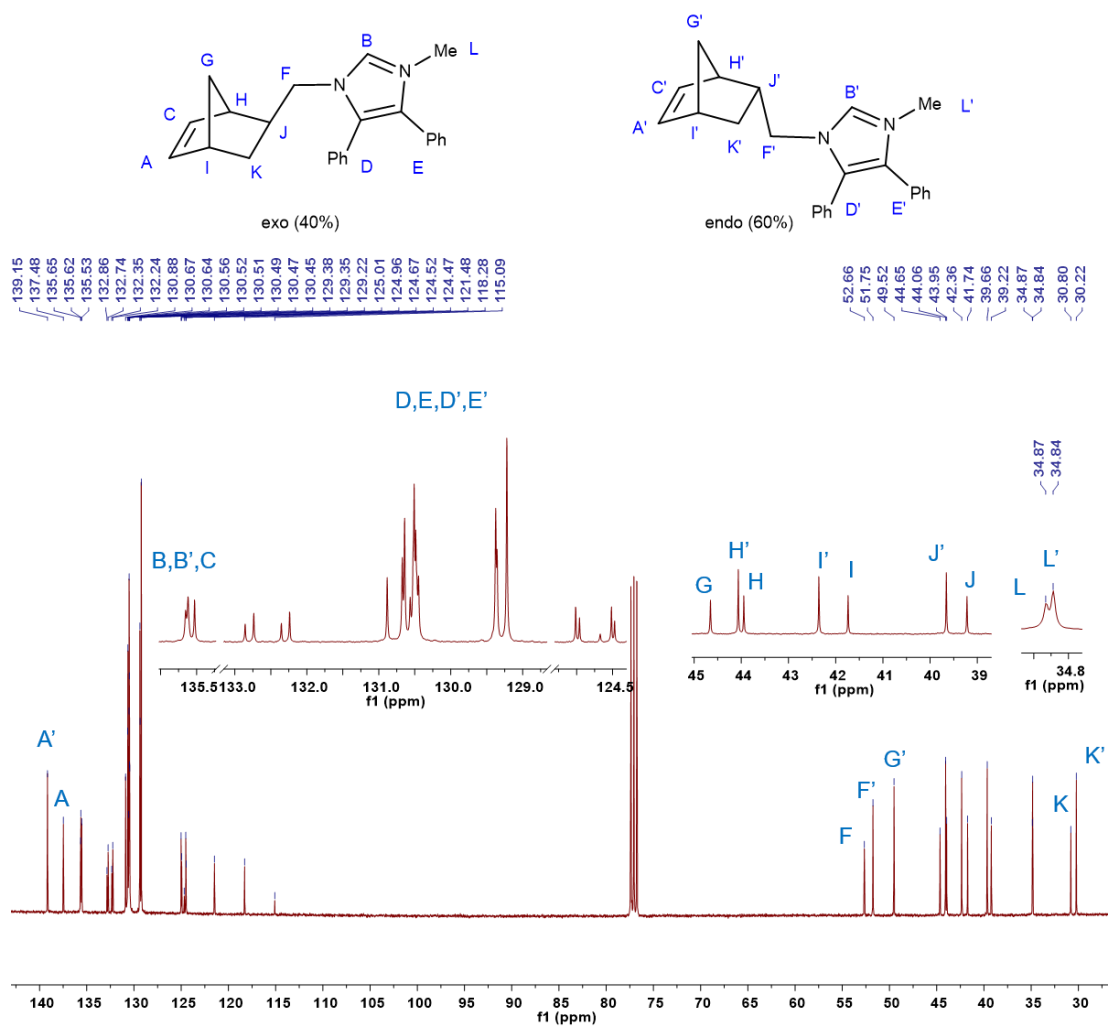


Figure S55. Assignment of ^{13}C NMR spectrum of S11 (*endo:exo* = 60:40).

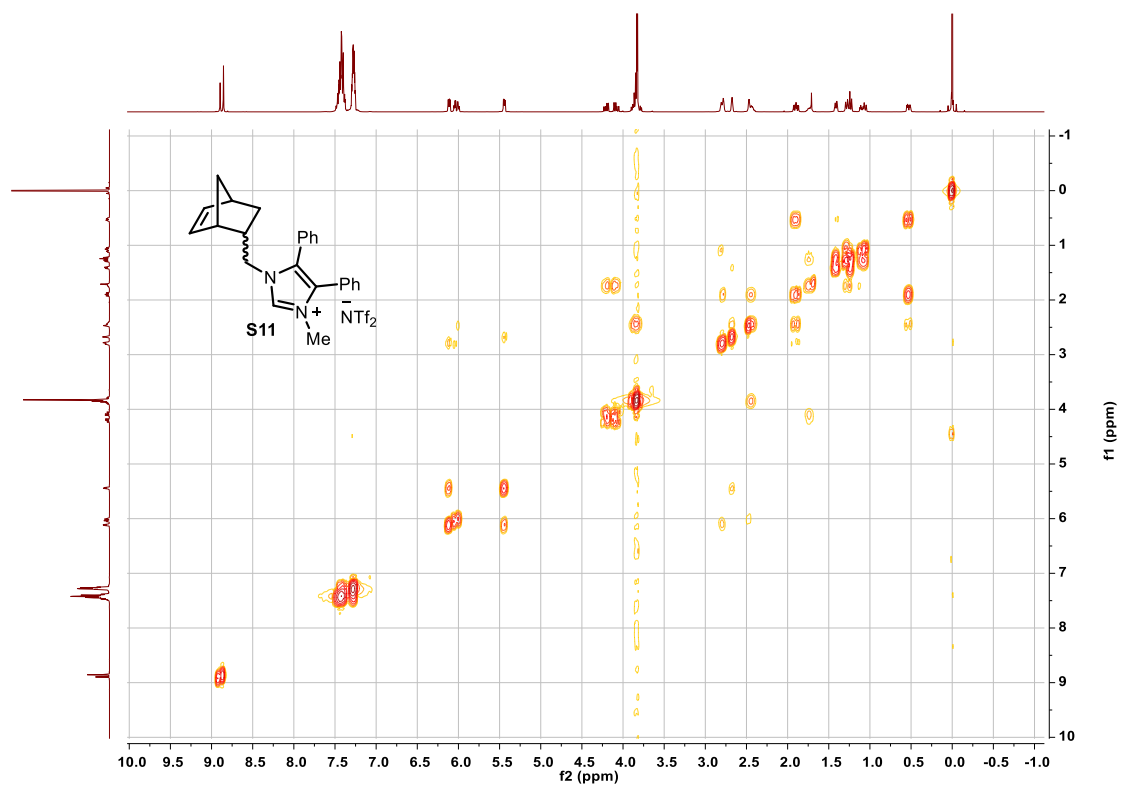


Figure S56. COSY spectrum of **S11** (*endo:exo* = 60:40).

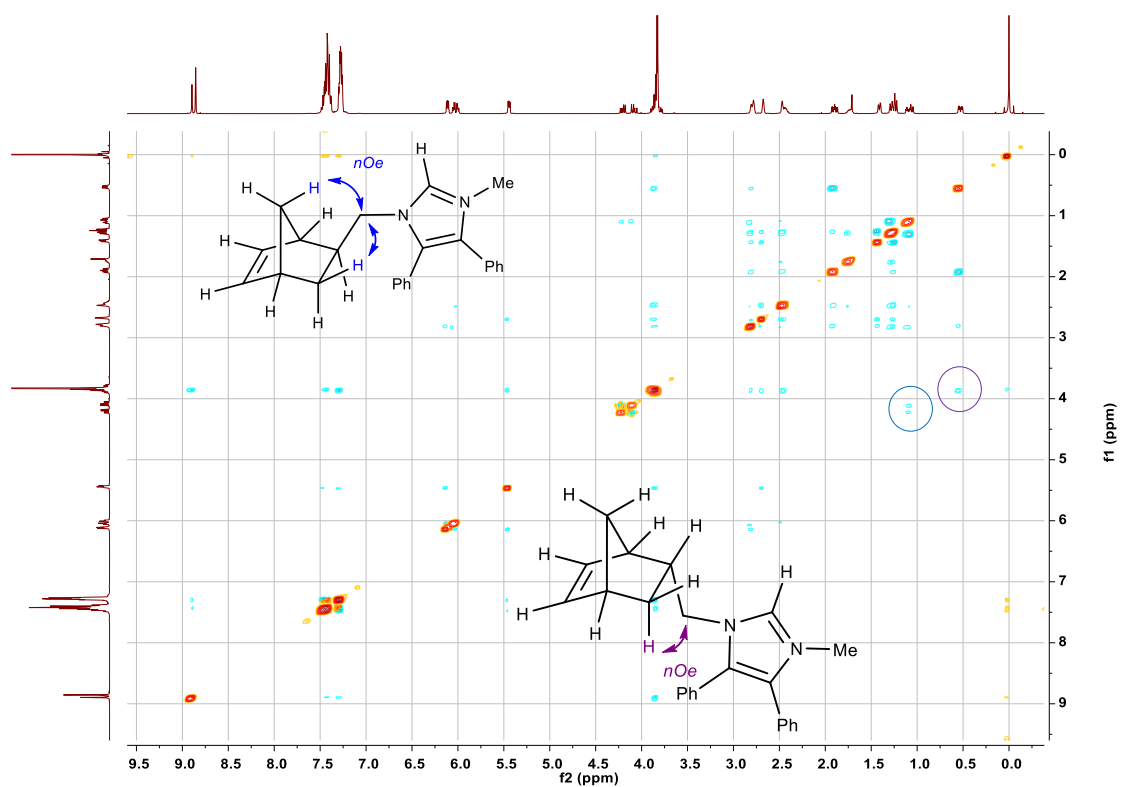


Figure S57. NOESY spectrum of **S11** (*endo:exo* = 60:40).

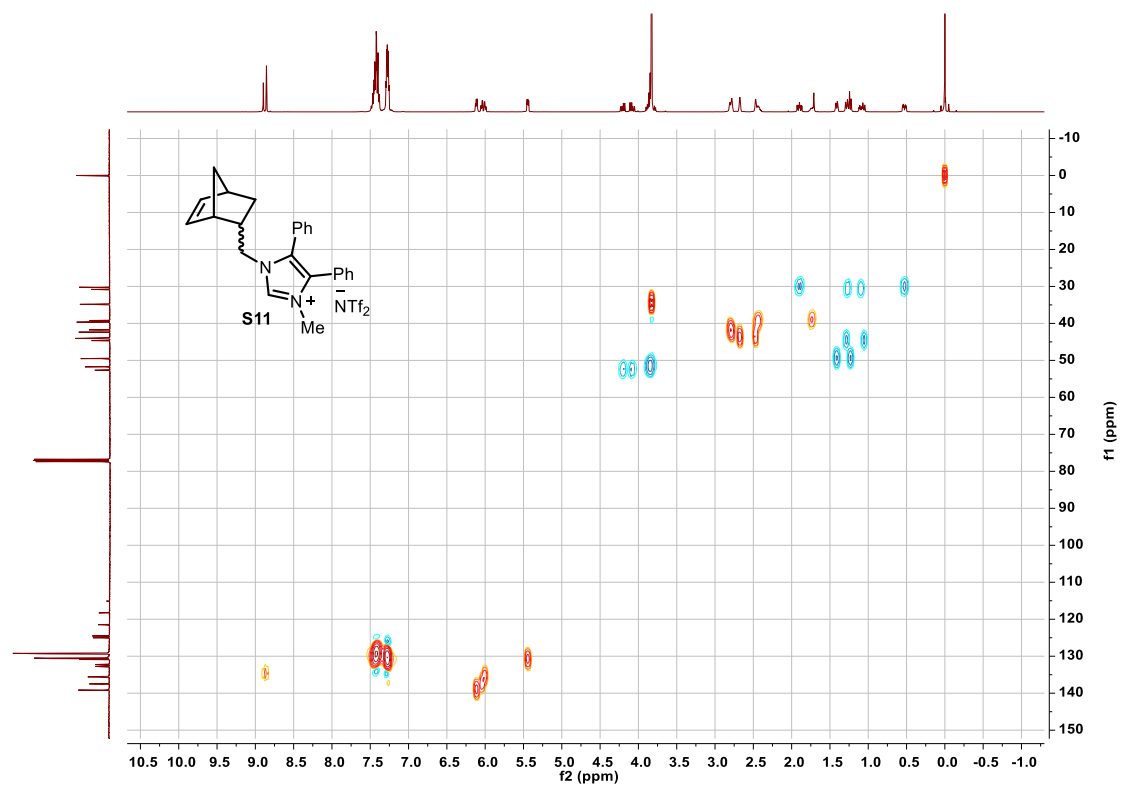


Figure S58. HSQC spectrum of S11 (*endo:exo* = 60:40).

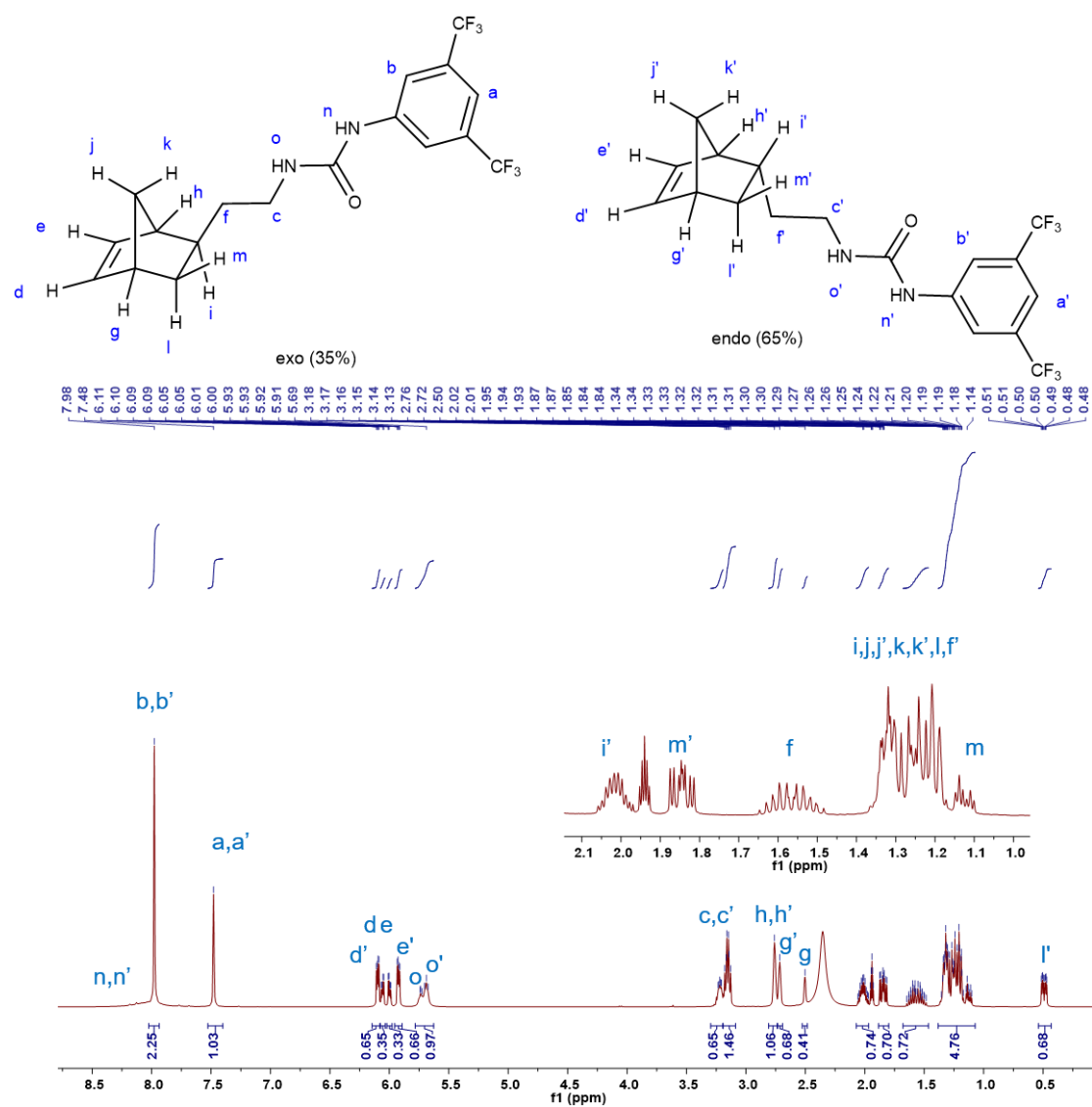


Figure S59. Assignment of ^1H NMR spectrum of S2 (*endo:exo* = 65:35).

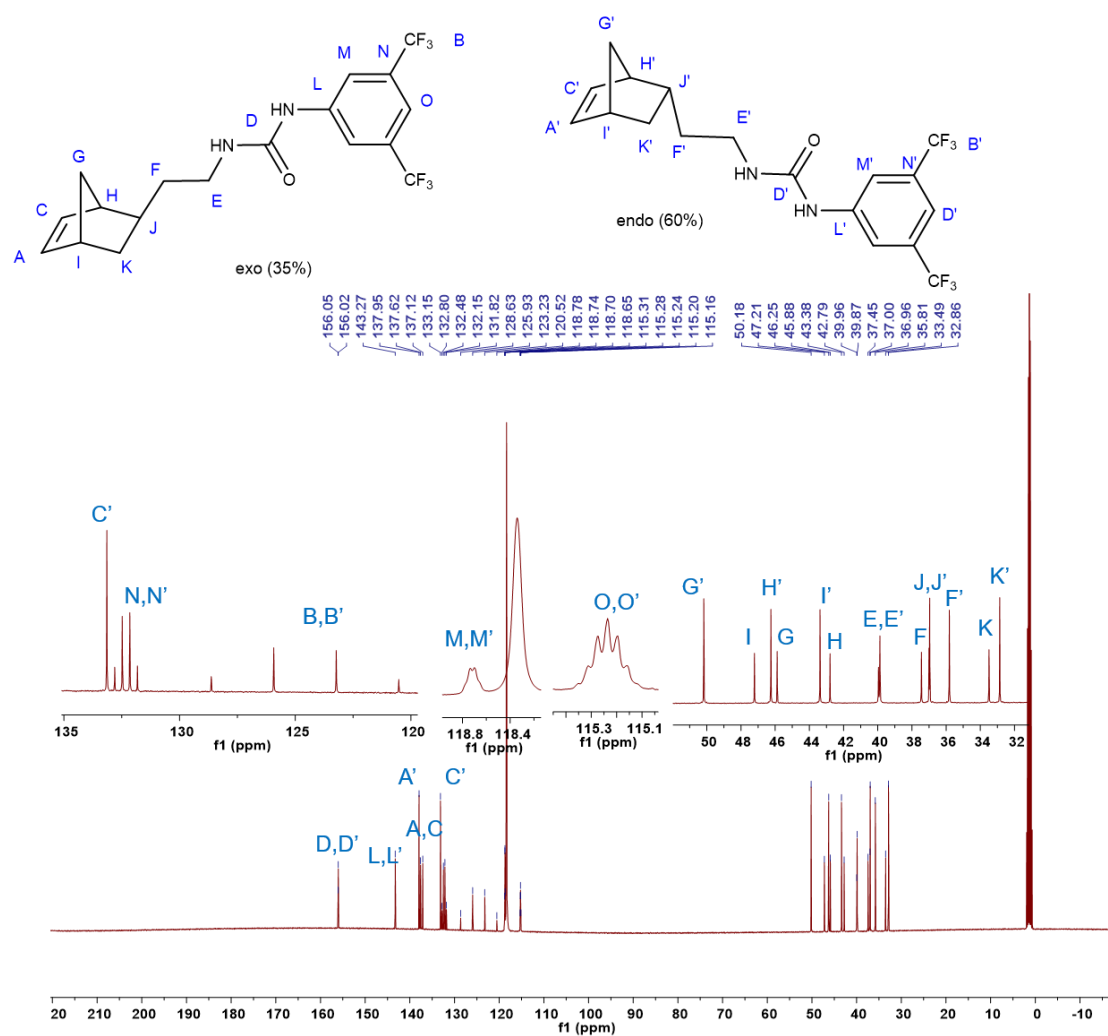


Figure S60. Assignment of ^{13}C NMR spectrum of S2 (*endo:exo* = 65:35).

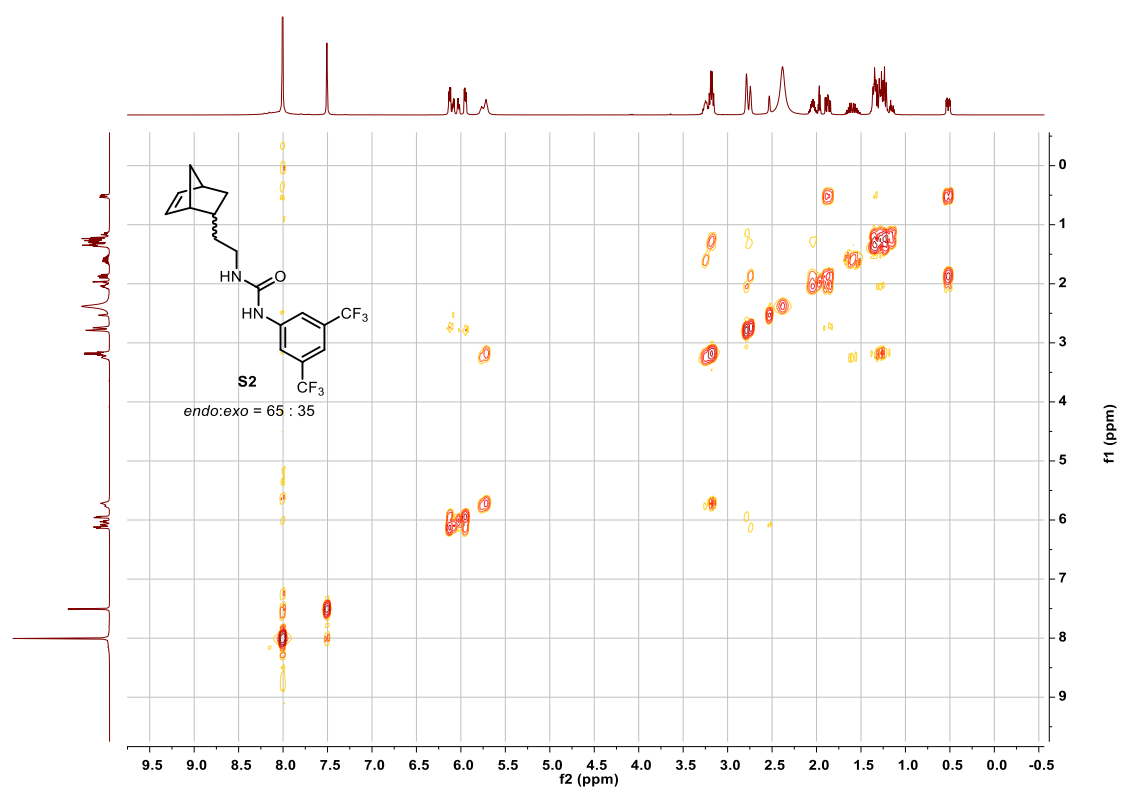


Figure S61. COSY spectrum of S2 (*endo:exo* = 65:35).

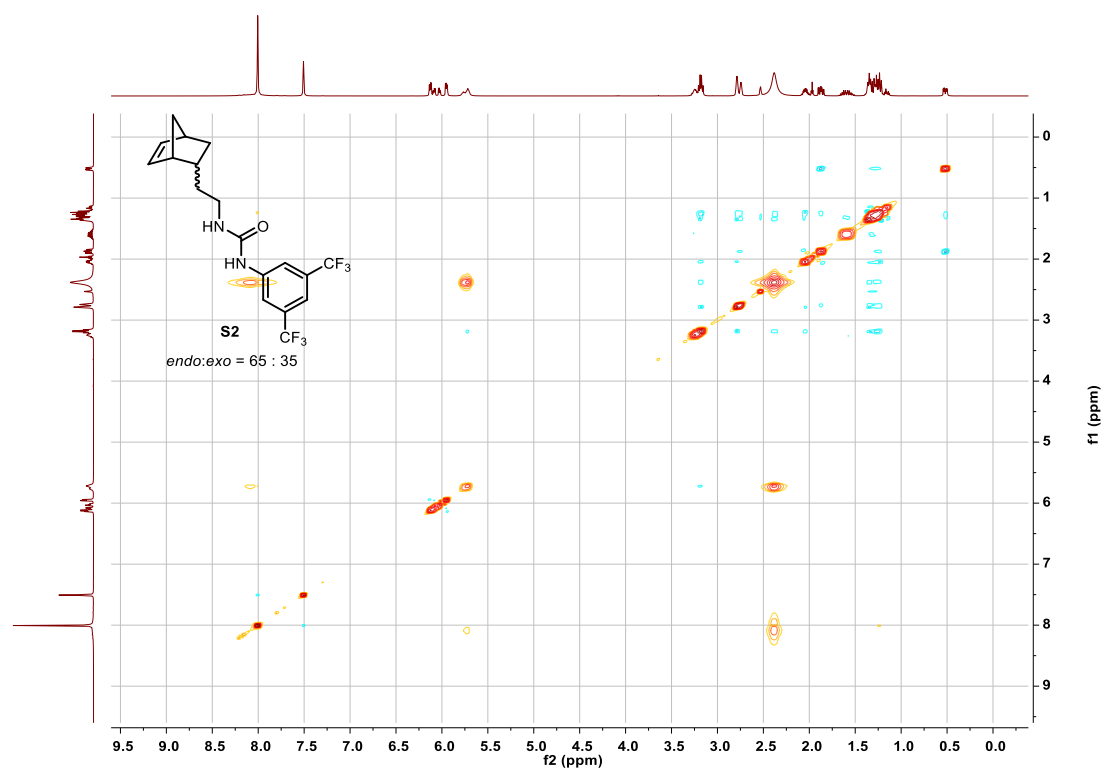


Figure S62. NOESY spectrum of S2 (*endo:exo* = 65:35).

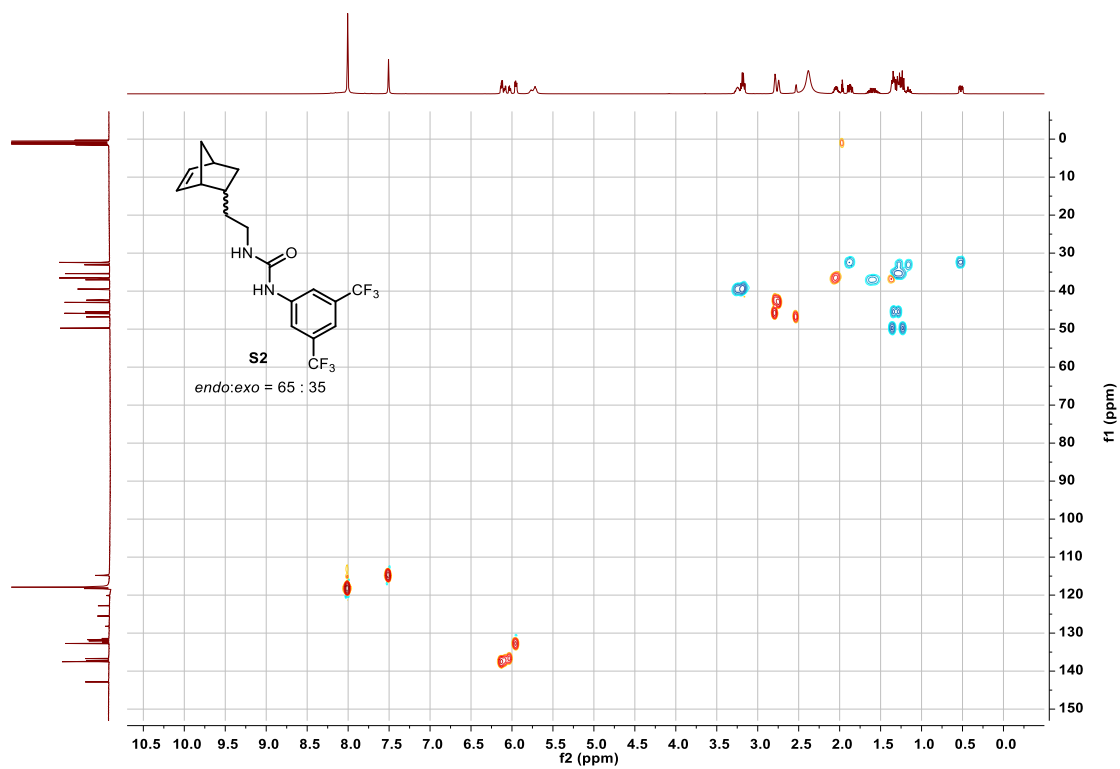
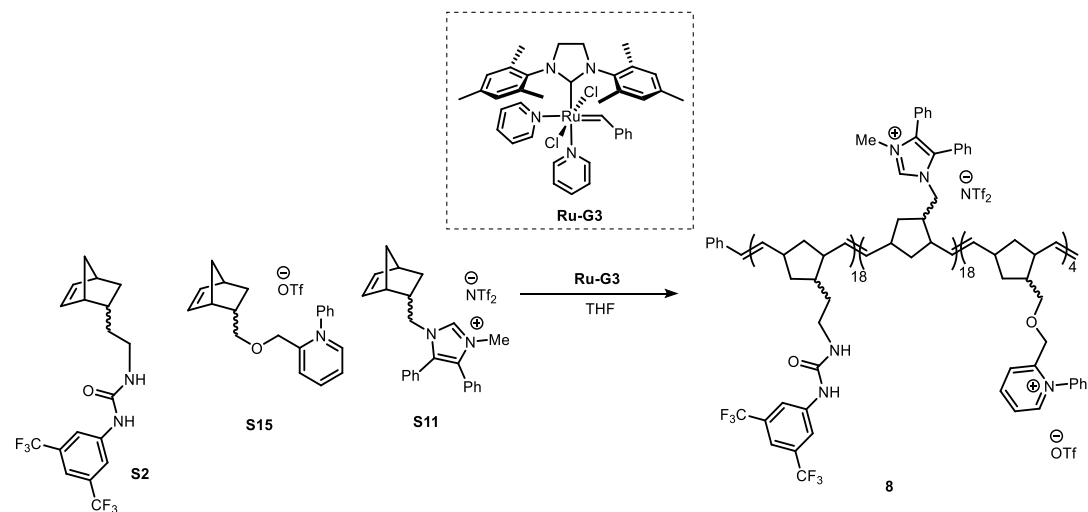


Figure S63. HSQC spectrum of **S2** (*endo:exo* = 65:35).

11. Synthesis and characterization data of (co)polymers

General procedure C for synthesizing (co)polymers:



A mixture of **S2** (52.9 mg, 0.135 mmol), **S11** (83.8 mg, 0.135 mmol), **S15** (14.1 mg, 0.03 mmol), and Grubbs third-generation catalyst **Ru-G3** (5.45 mg, 0.0075 mmol) in anhydrous tetrahydrofuran (3 mL) was stirred at room temperature for 24 hours at an argon atmosphere. The reaction mixture was quenched by ethyl vinyl ether (200 μ L) and then stirred for 2 hours. Dichloromethane (3 mL) and SiliaMetS DMT was added, and the mixture was stirred at room temperature for 3 hours and filtered. Treatment of SiliaMetS DMT was repeated to remove residual Ru complexes. The resulting mixture was evaporated and dissolved in dichloromethane/tetrahydrofuran and then precipitated in pentane. The white solid was collected and dried in vacuum for 24 hours to obtain the polymer product (70% yield).

Quantification of the residual Ru after the SiliaMetS DMT treatment

A sample of purified polymer **8** (2.1 mg) was weighed on a microbalance, digested by shaking overnight with 1 g concentrated nitric acid (70%), and sonicated for 3 hours. The sample was then diluted by Milli-Q water to 2% nitric acid solution (35 mL). The sample was measured twice, and the intensities were obtained for ruthenium isotopes 99, 101, and 102. The intensity of pure 2% nitric acid was subtracted from the sample intensities to give the net intensities. To determine the actual concentration of ruthenium in the samples, the net intensities were compared to that of ruthenium standards. The standards were obtained by diluting a ruthenium standard of 1000 mg/L Ru in 7% HCl (Certipur®, 1.70347.0100) with 2% nitric acid. The amount of Ru was determined to be 13 ± 2 μ g/L, which corresponds to 170 ± 20 ppm. This result indicated that the majority of Ru ($\sim 97\%$) was removed by the SiliaMetS DMT treatment.

¹H NMR characterizations of (co)polymers

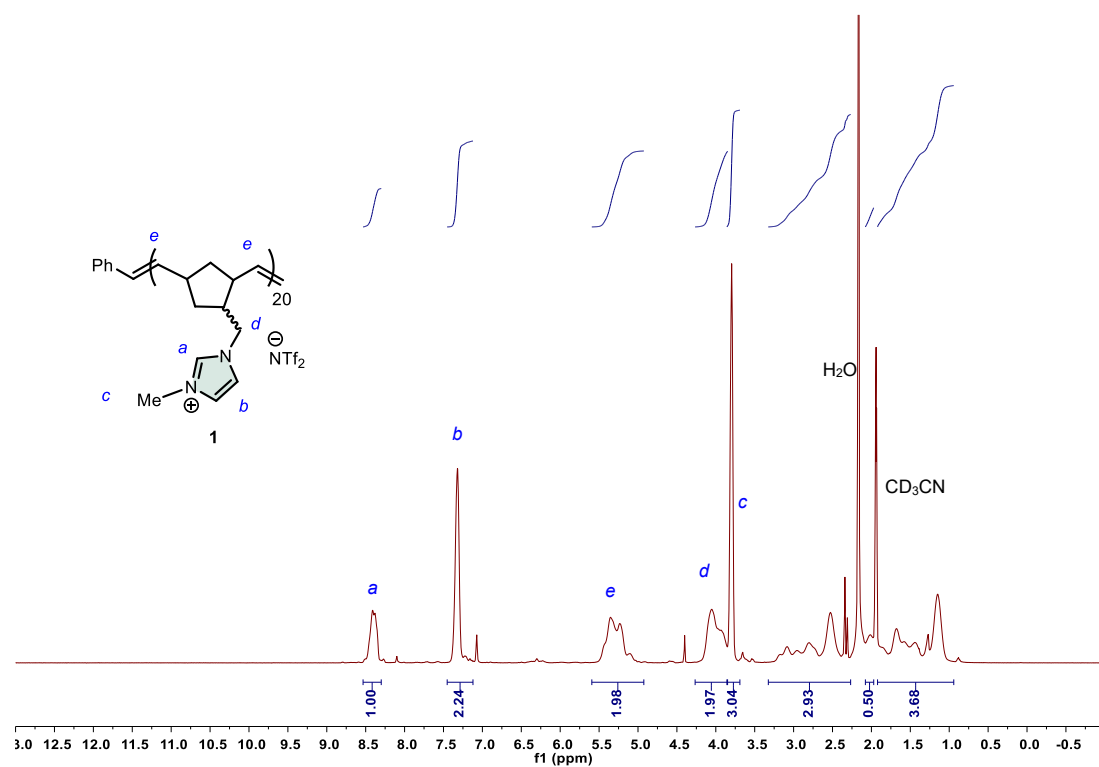


Figure S64. ¹H NMR spectrum of **1**.

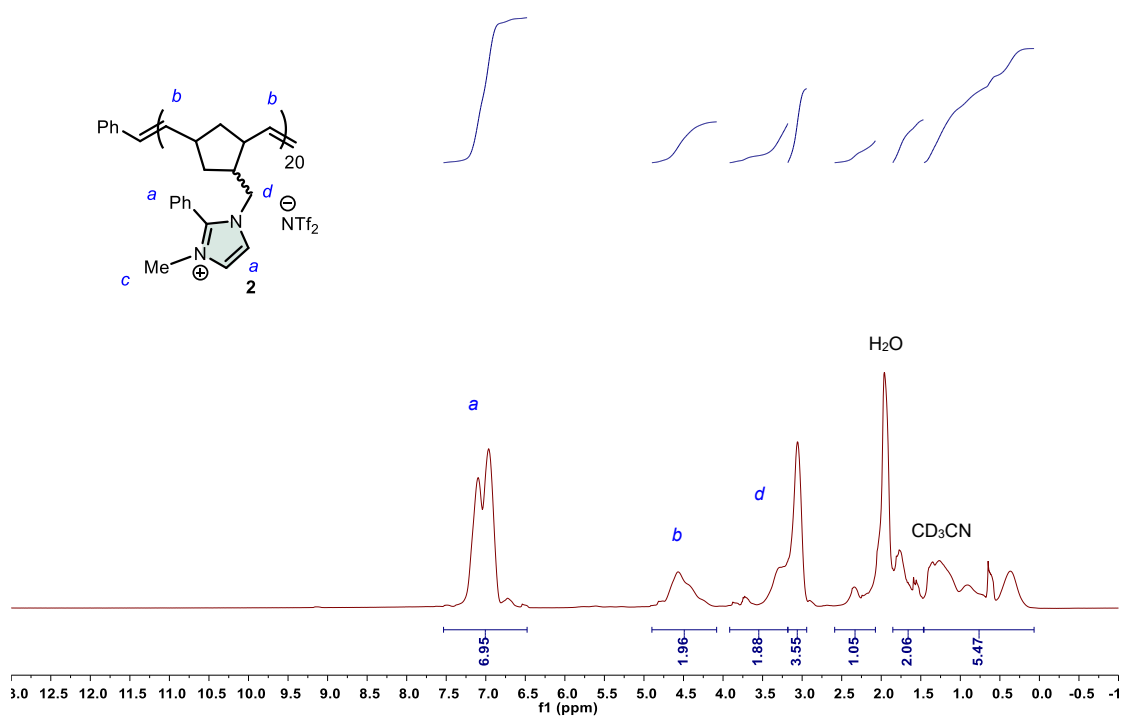


Figure S65. ¹H NMR spectrum of **2**.

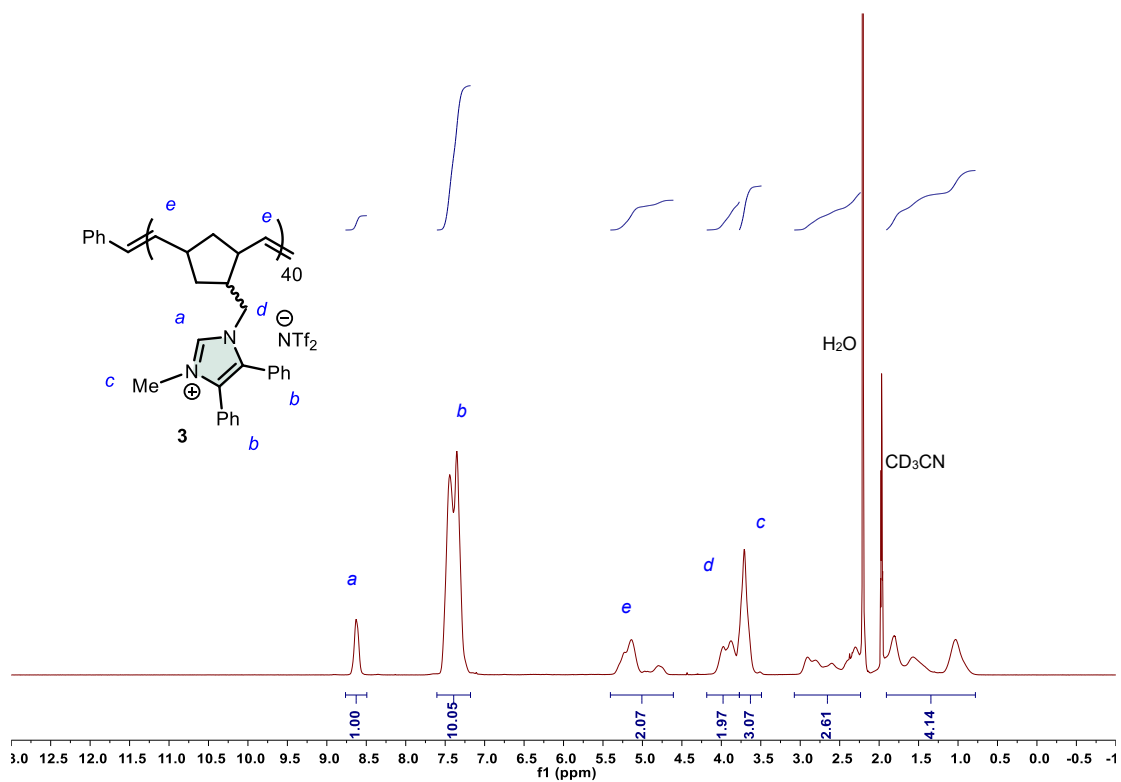


Figure S66. ¹H NMR spectrum of **3**.

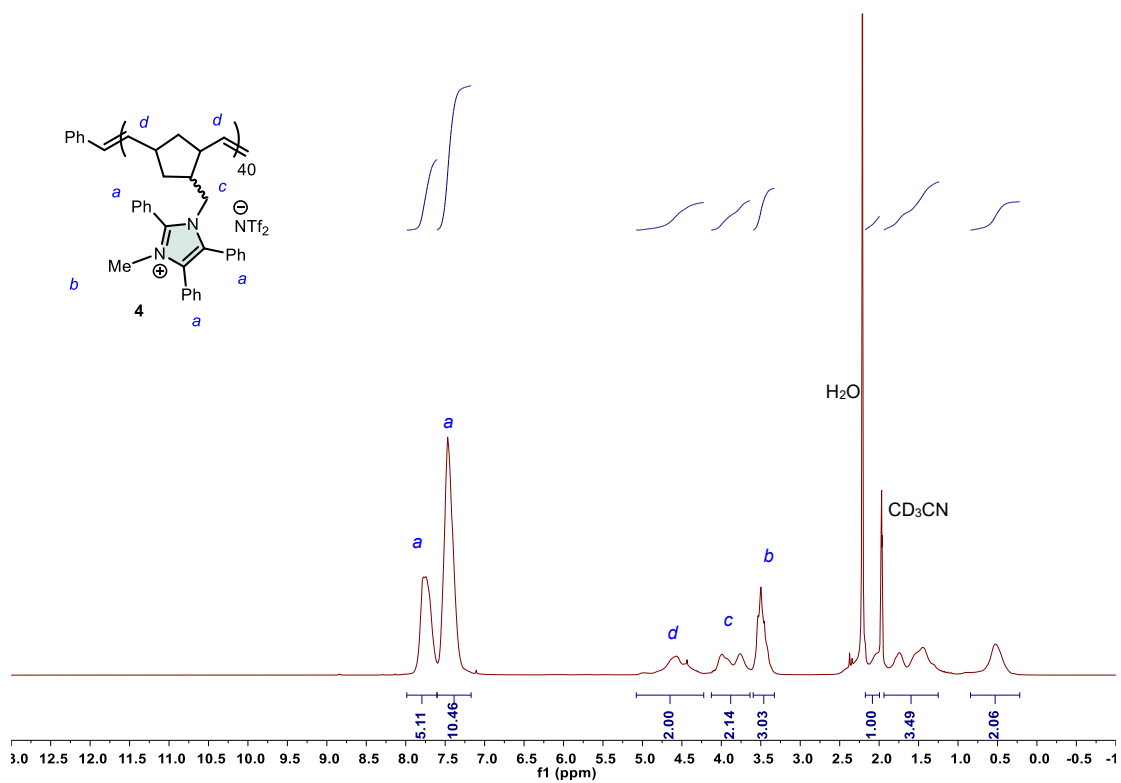


Figure S67. ¹³C NMR spectrum of **2**.

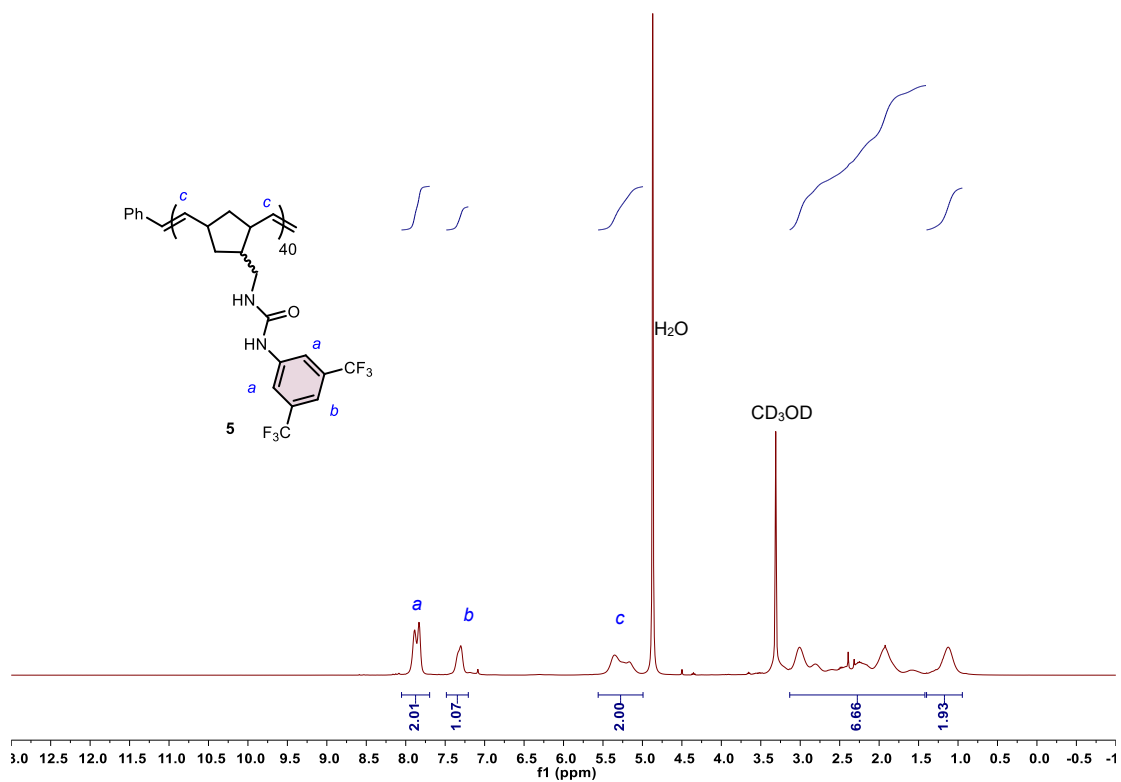


Figure S68. ¹H NMR spectrum of **5**.

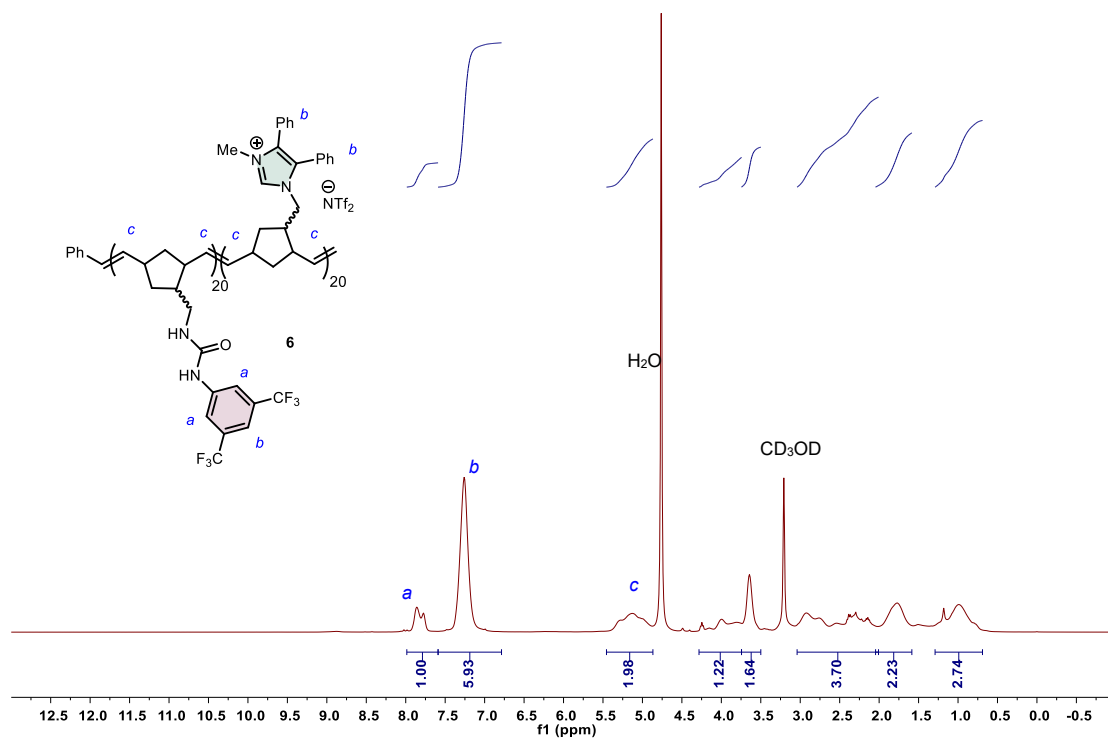


Figure S69. ¹H NMR spectrum of **6**.

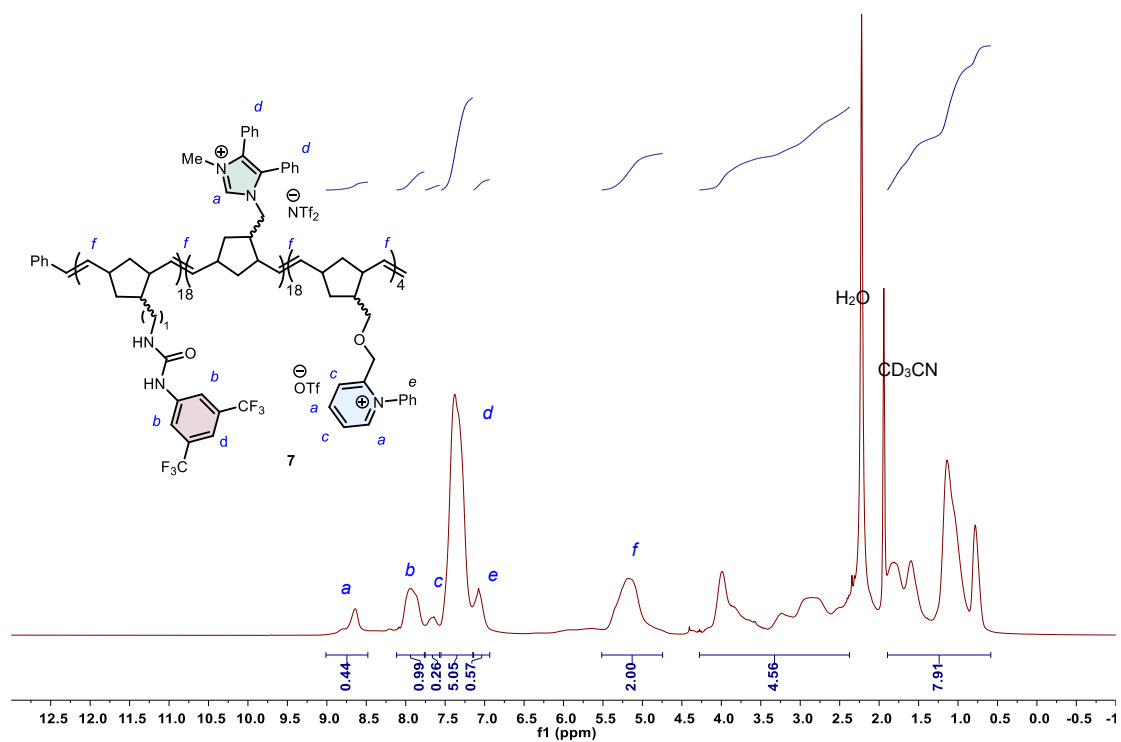


Figure S70. ¹H NMR spectrum of **7**.

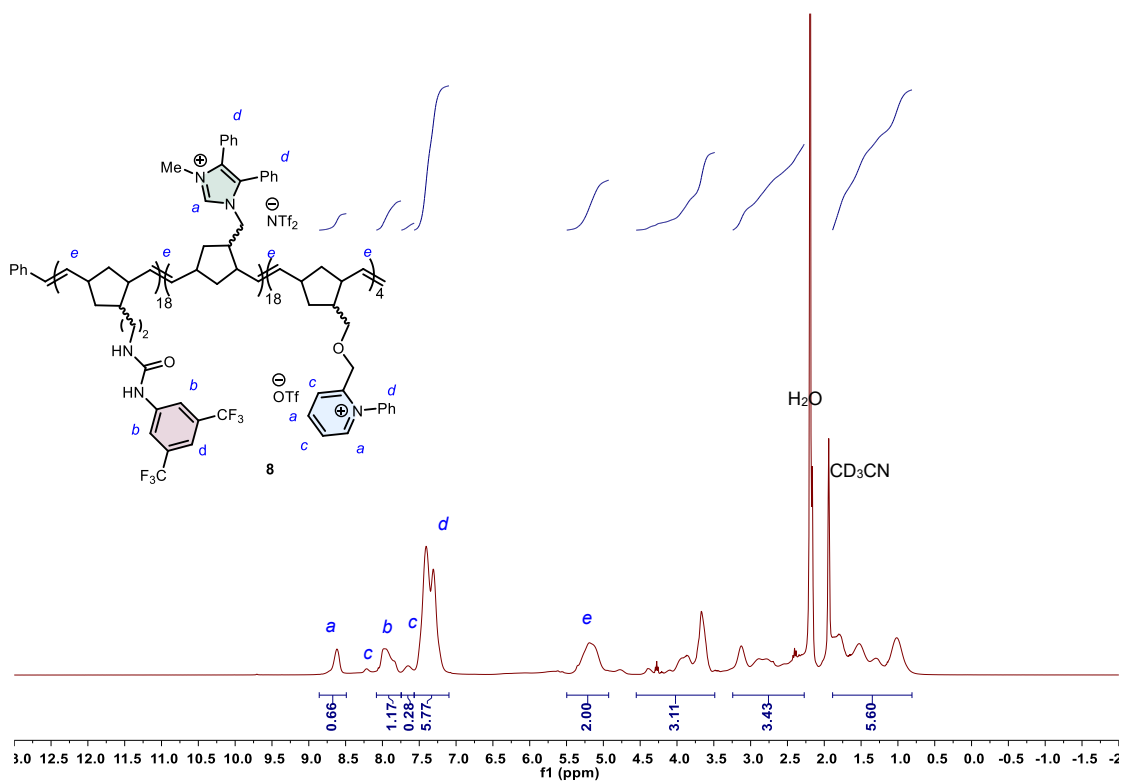


Figure S71. ¹H NMR spectrum of **8**.

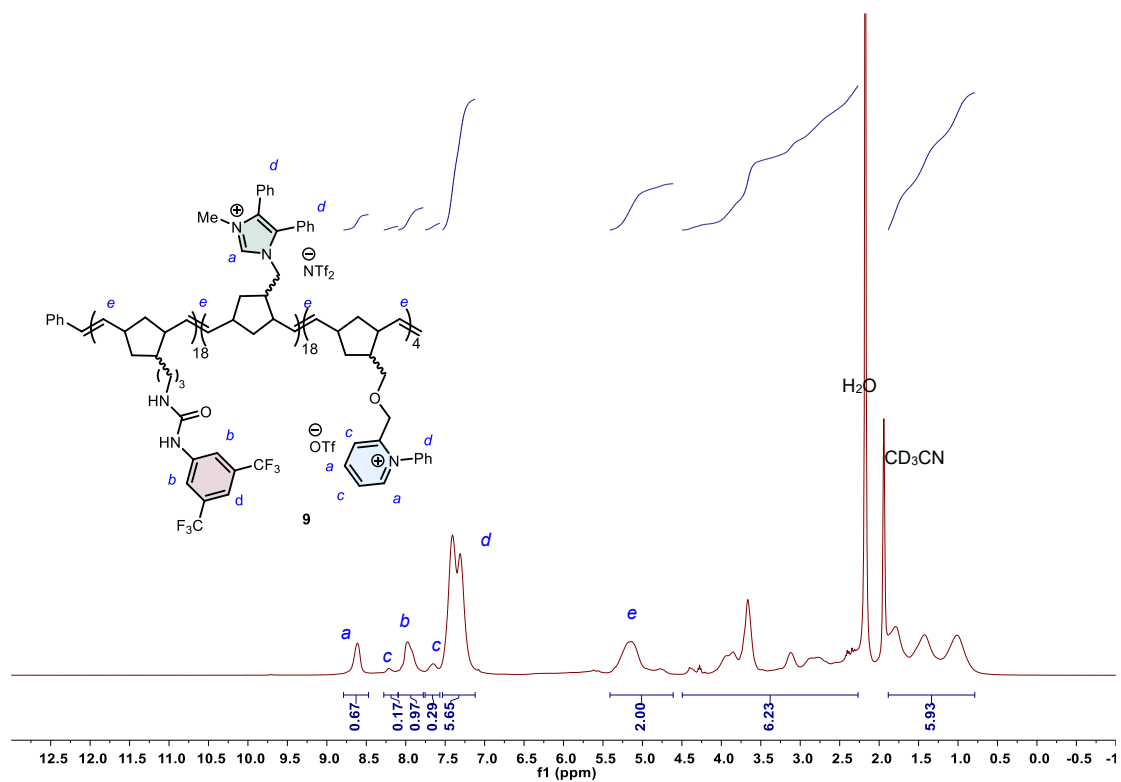


Figure S72. ^1H NMR spectrum of **9**.

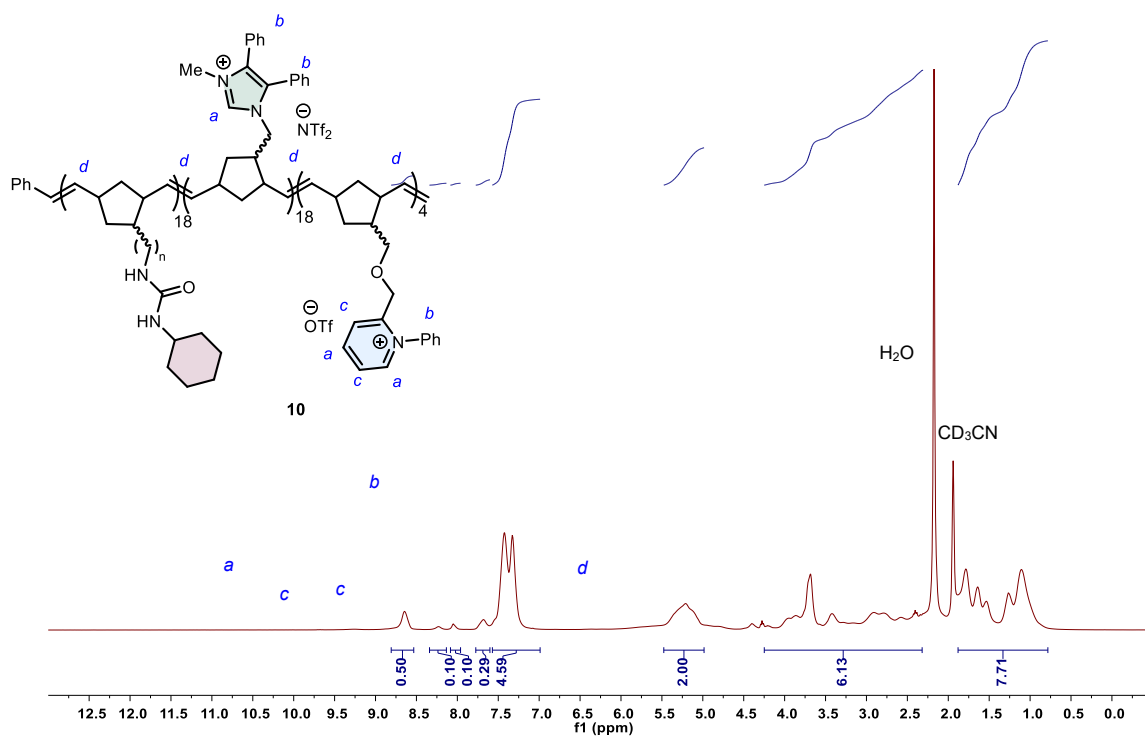


Figure S73. ^1H NMR spectrum of **10**.

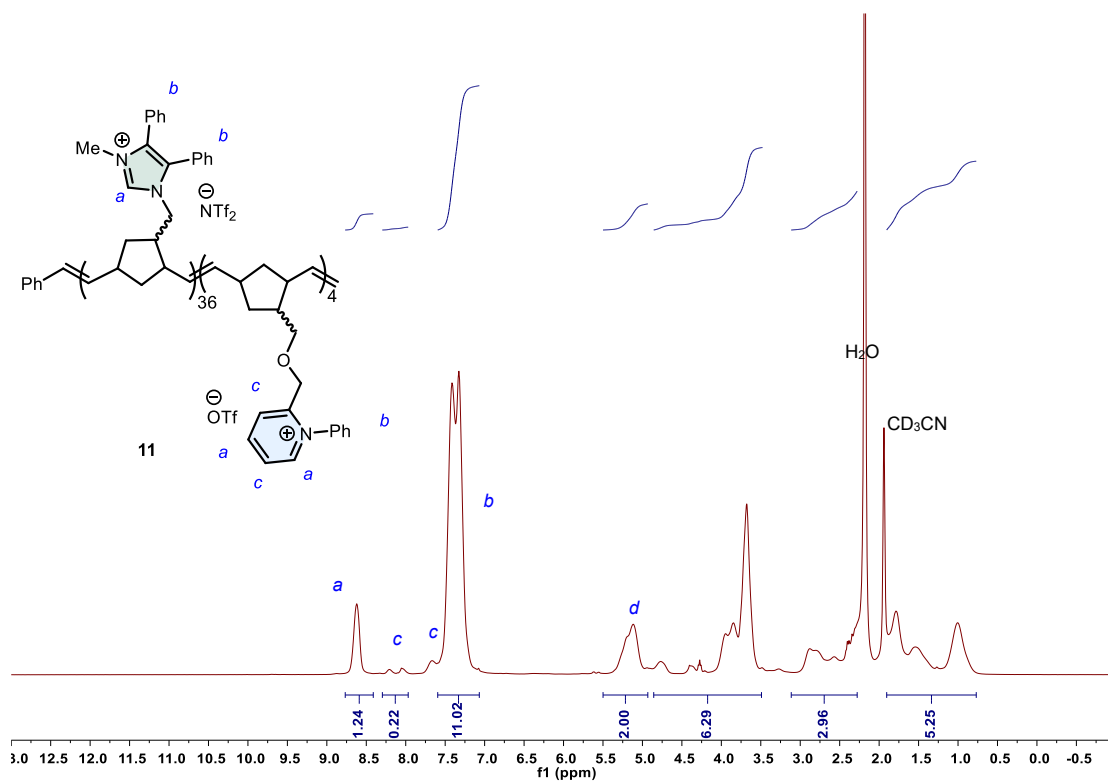


Figure S74. ¹H NMR spectrum of **11**.

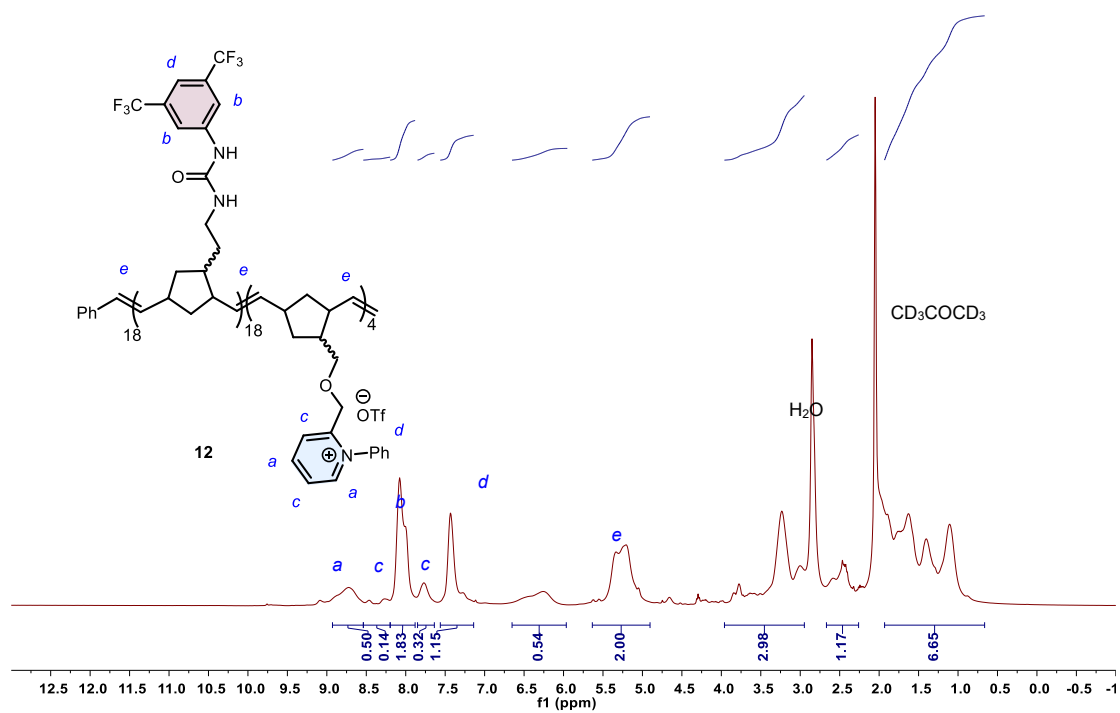


Figure S75. ¹H NMR spectrum of **12**.

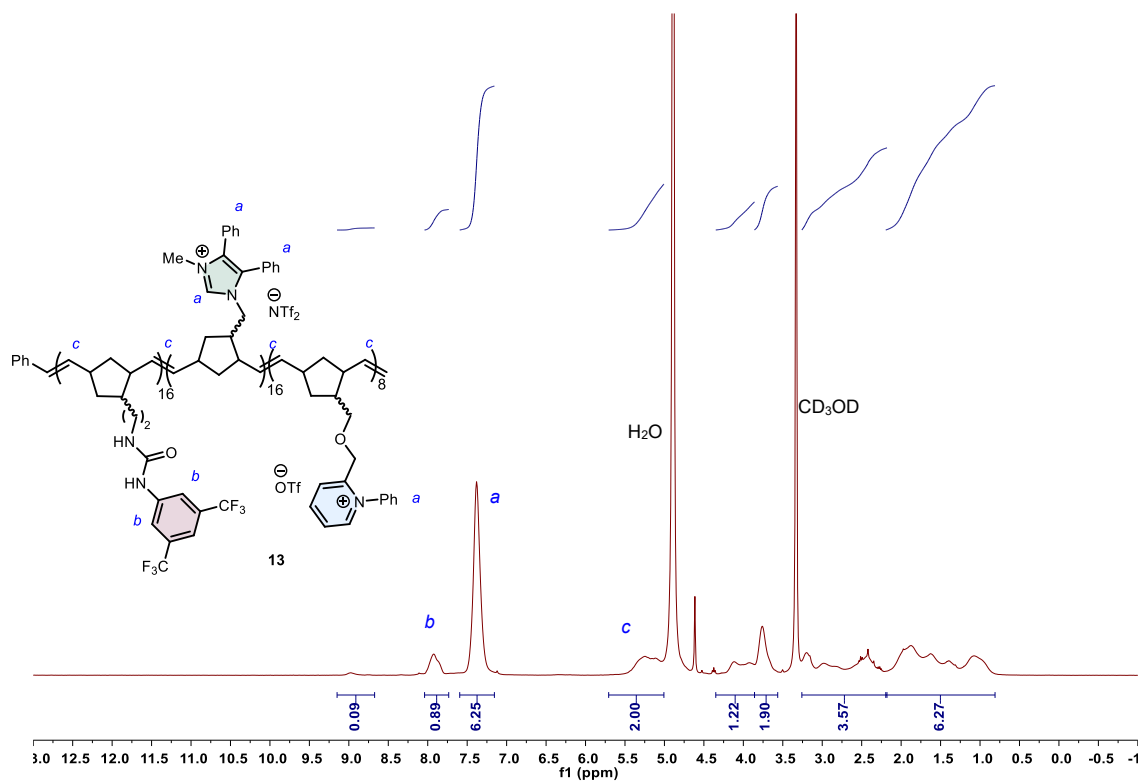


Figure S76. ¹H NMR spectrum of **13**.

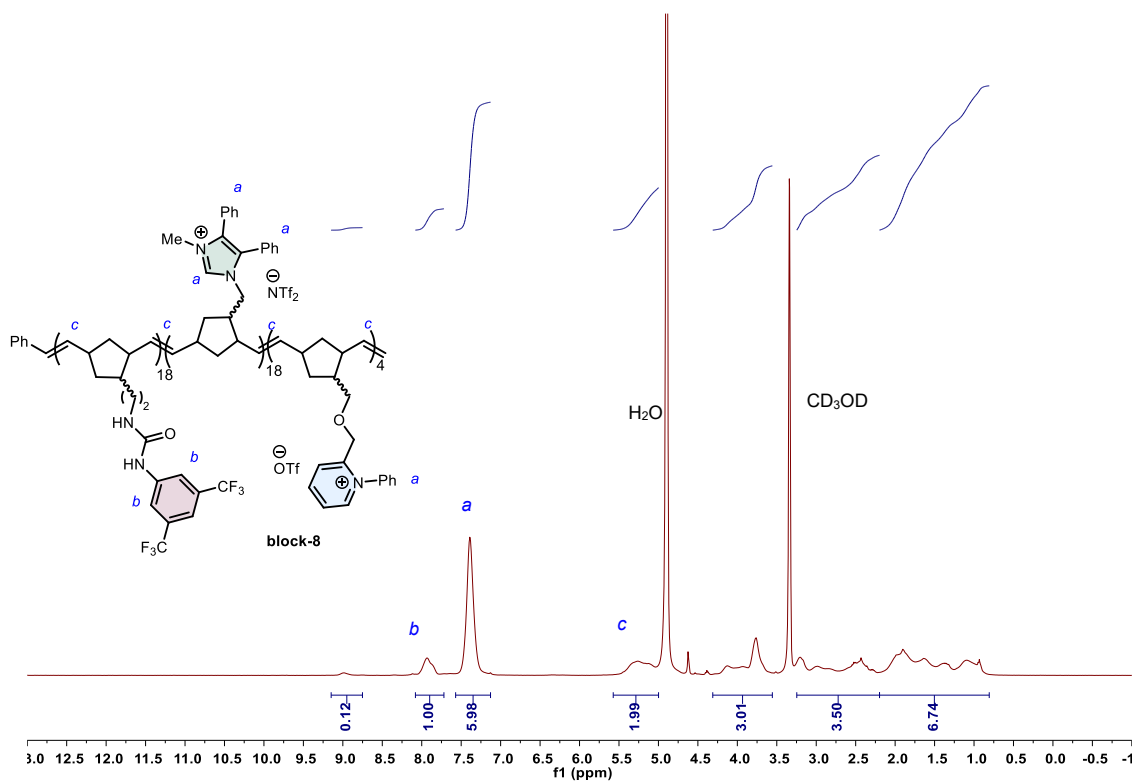


Figure S77. ¹H NMR spectrum of **block-8**.

MALDI-TOF characterizations of polymers

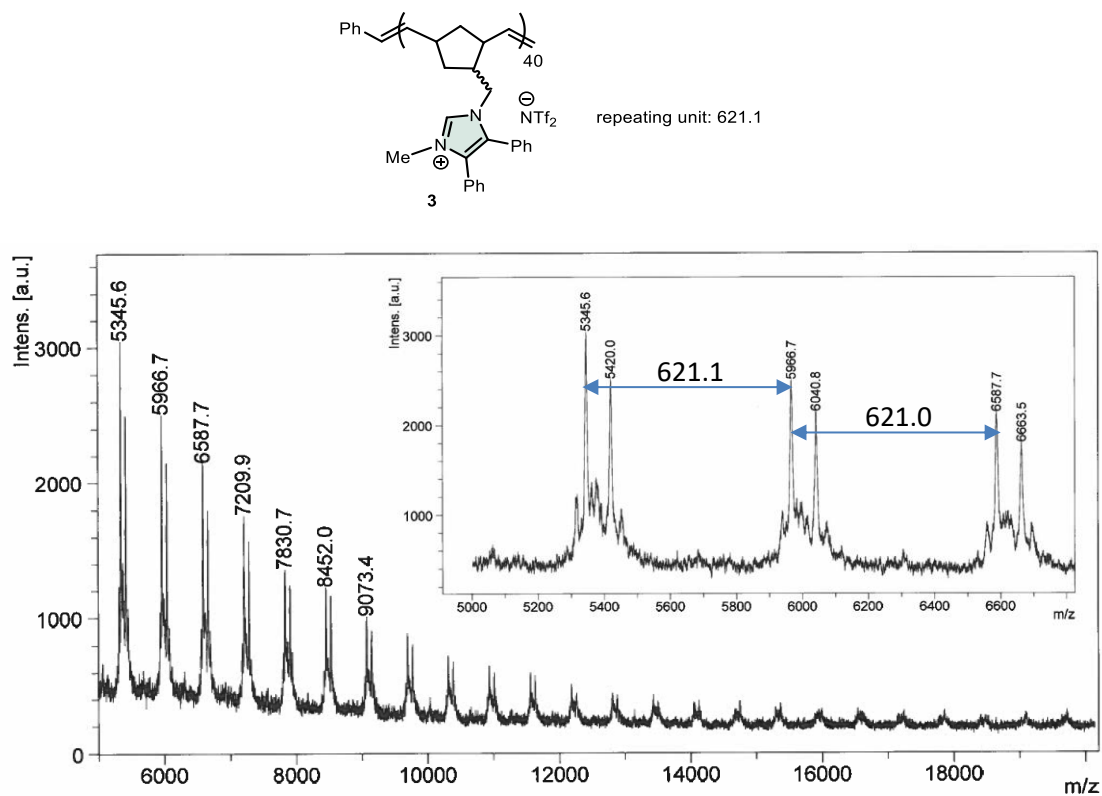


Figure S78. MALDI-TOF of polymer **3** with DCTB matrix

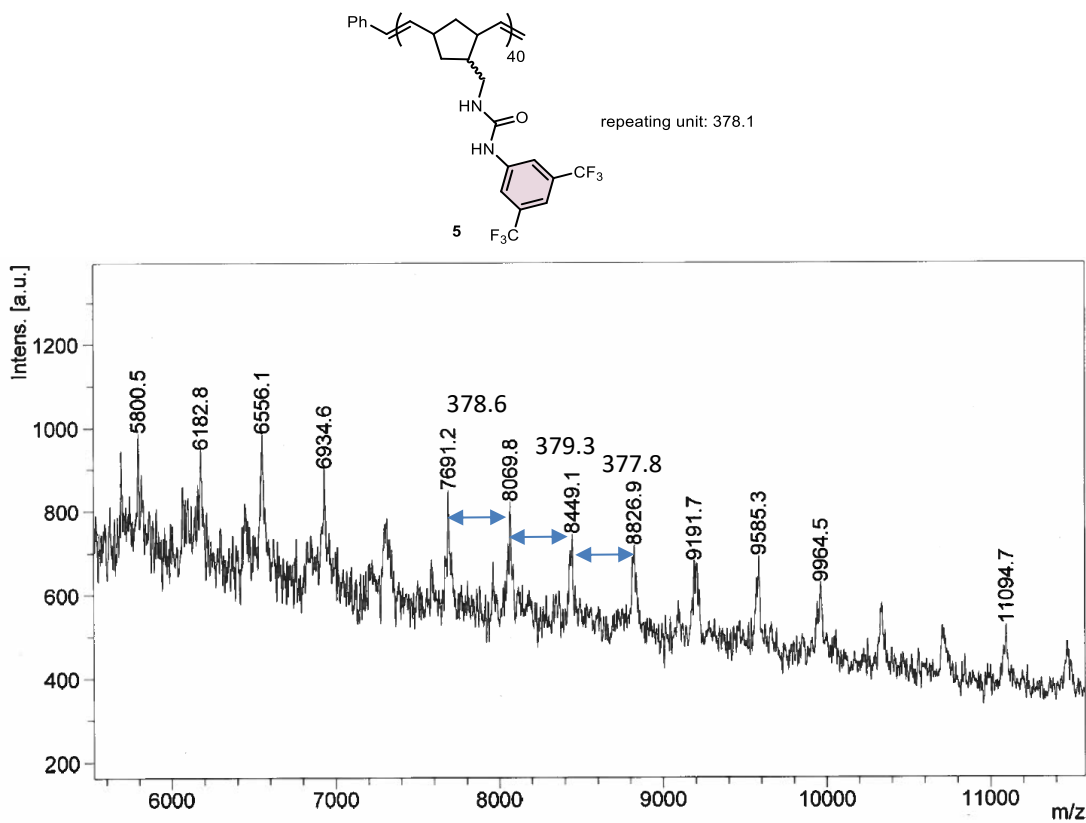
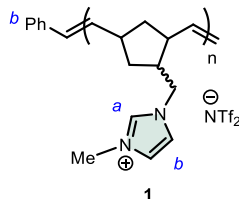


Figure S79. MALDI-TOF of polymer **5** with DCTB matrix

SEC traces of polymers

The molecular weights of polymers were determined by SEC, except for polymer **1**. Polymer **1** has low solubility in tetrahydrofuran, probably due to strong intermolecular electrostatic interaction. The molecular weight of polymer **1** was determined by its ^1H NMR.



The integration ratio of proton a (8.4 ppm) and proton b (7.3 ppm) is 1 : 2.24, therefore we can obtain the degree of polymerization n by following equation, which matches the theoretical value:

$$\frac{2n + 5}{n} = 2.24$$

$$\therefore n = 20.8$$

Table S3. Measurement of MW using SEC

polymer	PDI	SEC MW (kDa)	Theoretical MW (kDa)
2	1.02	22.1	11.0
3	1.02	31.8	24.9
4	1.06	34.6	28.0
5	1.04	21.9	15.2
6	1.09	23.0	20.0
7	1.07	30.6	19.9
8	1.09	29.7	20.1
9	1.39	36.1	20.4
10	1.09	29.9	17.5
11	1.02	27.5	24.2
12	1.01	34.9	16.0
13	1.25	30.0	19.9

Typical SEC traces can be found below:

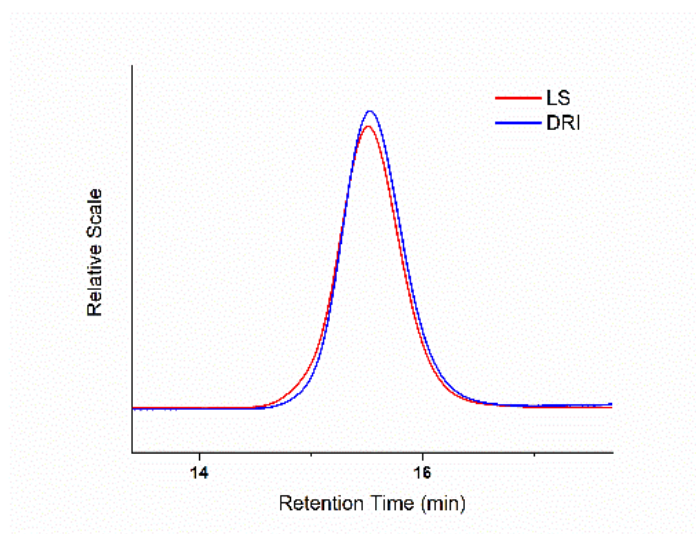


Figure S80. SEC trace of polymer **3**

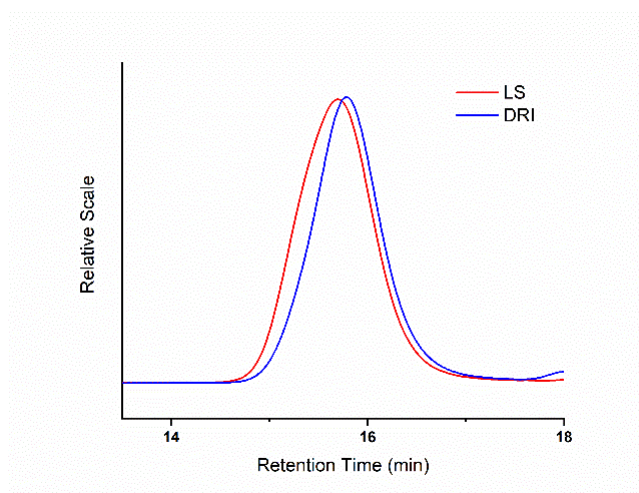


Figure S81. SEC trace of polymer **8**

12. References

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